REMARKS

Status of the Claims:

Claims 1 – 28 and 31 – 34 are currently pending.

Claims 1 – 34 are currently rejected.

 Claims 11, 12, 29 and 32 are rejected under 35 U.S.C. § 112.

 . Claims 1 – 34 are rejected under 35 U.S.C. § 103.

Claims 29 and 30 are currently cancelled.

Claims 1 – 11, 13, 14, 16, 18 – 24, 27, 28 and 31 – 34 are currently amended.

Amendments to the Claims:

No new matter has been introduced by way of the claim amendments.

Claim 1 is amended in step a) to delete the limitation of a functionalized species on the sidewall of the carbon nanotubes. Claim 1 is amended in step a)(ii) to recite that the carbon nanotubes comprise nucleation sites operable for initiating a polymerization reaction selected from the group consisting of anionic polymerization and ring opening polymerization. The amendments in step a)(ii) provide clarity, and support can found in at least claim 1 as originally filed. Claim 1 is amended in step b) to recite dispersing the functionalized carbon nanotubes in the solvent. The phrase 'said aryl halide' has been deleted in order to make this step commensurate in scope with the rest of the claim. Claim 1 is amended in step c) to place the elements (i), (ii) and (iii) in a Markush group. Claim 1 is also amended in step c) to recite that the at least one reagent reacts with the functionalized carbon nanotubes to form a polymerizable species. The polymerizable species is selected from the group consisting of an aryl-lithium species, an aryl-metal bond species and initiator groups. The initiator groups are formed by deprotonation of the nucleation sites. The amendments in step c) clarify details concerning Applicants' method, and support can be found in at least claim 1 as originally filed and paragraphs [0012], [0026] and [0028] of the instant specification. Claim 1 is amended in step e) to recite a polymerization reaction between the monomer and the polymerizable species. The polymerization reaction is recited as being selected from a Markush group consisting of anionic

polymerization and ring opening polymerization. The polymerization reaction is recited as occurring between the monomer and the polymerizable species, rather than between the monomer and the functionalized carbon nanotubes as previously written, in order to clarify that a transformation of the functionalized carbon nanotubes has occurred in order to affect the polymerization reaction.

Claim 2 is presently amended in step c) to reflect that the alkyllithium species reacts with the aryl halide functionalized carbon nanotubes to form an aryl-lithium species comprising aryl-lithium bonds. Support for this amendment may be found in at least paragraph [0012] and Figure 1 of the instant specification. Claim 2 is also amended in step c) to correct a minor typographical error. Claim 2 is presently amended in step e) to recite a polymerization reaction between the monomer and the aryl-lithium species. The polymerization reaction is recited as being selected from a Markush group consisting of anionic polymerization and ring opening polymerization. The polymerization reaction is recited as occurring between the monomer and the aryl-lithium species, rather than between the monomer and the functionalized carbon nanotubes as previously written, in order to clarify that a transformation of the functionalized carbon nanotubes has occurred in order to affect the polymerization reaction.

Claim 3 is presently amended in step c) to reflect that the metal reacts with the aryl halide functionalized carbon nanotubes to form an aryl-metal species comprising aryl-metal bonds. Support for this amendment may be found in at least paragraph [0012] and Figure 2 of the instant specification. Claim 3 is presently amended in step e) to recite a polymerization reaction between the monomer and the aryl-metal species. The polymerization reaction is recited as being selected from a Markush group consisting of anionic polymerization and ring opening polymerization. The polymerization reaction is recited as occurring between the monomer and the aryl-metal species, rather than between the monomer and the functionalized carbon nanotubes as previously written, in order to clarify that a transformation of the functionalized carbon nanotubes has occurred in order to affect the polymerization reaction.

Claim 4 is presently amended to recite that the metal is selected from the indicated Markush group. The phrase 'comprises a substance' has been deleted to reflect that it is the metallic elements and combinations thereof that are claimed. Support for this amendment may

be found in the instant specification in at least paragraph [0026]. Claim 4 is also amended to correct a minor grammatical error by deleting the word 'include'.

Claim 5 is presently amended for clarity. As amended, claim 5 recites that the aryl-metal bonds are aryl-Mg bonds, which comprise a Grignard species.

Claim 6 is presently amended for purposes of clarity and antecedent support. Additionally, the preamble of claim 6 has been rewritten for purposes of clarity.

The preamble of claim 7 has been rewritten for purposes of clarity and to change 'methods' to 'method'.

Claim 8 is presently amended to correct a minor grammatical error. Additionally, the preamble of claim 8 has been rewritten for purposes of clarity and to change 'methods' to 'method'.

Claim 9 is presently amended to depend from any one of claims 1 or 2, rather than claims 1-4 or 5 as previously written. Claim 9 is also amended to change 'methods' to 'method'.

Claim 10 is presently amended in step a) to recite that the functionalized carbon nanotubes comprise nucleation sites for a polymerization reaction. Support for this amendment may be found in at least paragraphs [0021], [0027], [0028] and [0032] of the instant specification. The polymerization reaction is recited as being selected from a Markush group consisting of anionic polymerization and ring opening polymerization. Claim 10 is amended in step c) for purposes of clarity and for antecedent support. Claim 10 is presently amended in step e) to recite a polymerization reaction between the monomer and the initiator groups. The polymerization reaction is recited as occurring between the monomer and the initiator groups, rather than between the monomer and the functionalized carbon nanotubes as previously written, in order to clarify that a transformation of the functionalized carbon nanotubes has occurred in order to affect the polymerization reaction. Step e) also includes the limitation that the polymerization reaction is selected from a Markush group consisting of anionic polymerization and ring opening polymerization.

Claim 11 is presently amended to recite that the nucleation sites comprise at least one

element selected from the indicated Markush group. Support for the amendments to claim 11 may be found in at least paragraphs [0021] and [0027].

Claim 13 is presently amended to clarify that it is the nucleation sites that are on the sidewall of the functionalized carbon nanotubes. Support for this amendment may be found in at least paragraph [0032] of the instant specification. Additionally, the preamble of claim 13 has been rewritten for purposes of clarity.

The preambles of claims 14 and 16 have been rewritten for purposes of clarity.

Claim 18 and 19 are presently amended for purposes of clarity. Additionally, the preambles of claims 18 and 19 have been rewritten for purposes of clarity and to change 'methods' to 'method'.

The preambles of claims 20 – 23 have been rewritten for purposes of clarity and to change 'methods' to 'method'.

Claim 24 is presently amended for purposes of clarity and antecedent support. Additionally, the preamble of claim 24 has been rewritten for purposes of clarity and to change 'methods' to 'method'.

Claims 27 and 28 are presently amended for purposes of clarity and antecedent support. Additionally, the preamble of claims 27 and 28 have been rewritten for purposes of clarity and to change 'methods' to 'method'.

Claim 31 is presently amended to rewrite the claim as further comprising adding a polymerization catalyst to the solvent. Support for the amendments to claim 31 may be found in at least paragraph [0026] of the instant specification. Additionally, the preamble of claim 31 has been rewritten for purposes of clarity and to change 'methods' to 'method'.

Claim 32 is presently amended for purposes of antecedent support.

The preambles of claims 33 and 34 have been rewritten for purposes of clarity.

I.   Claim Rejections Under 35 U.S.C. § 112

Claims 11, 12, 29 and 32 stand rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which Applicants regard as the invention. Office Action item 3.

I.1.   *Rejection of Claim 11*

The Examiner asserts that claim 11 is indefinite and questions 'how the recited elements relate to the functionalized carbon nanotubes.'

Applicants have amended claim 10 and depending claim 11 in response to the indefiniteness rejection of claim 11. As amended, claim 10 recites that the functionalized carbon nanotubes comprise nucleation sites for a polymerization reaction, and the nucleation sites are deprotonated with a deprotonating agent to form initiator groups for the polymerization reaction. Claim 11, as amended, recites that the nucleation sites comprise at least one element selected from the group consisting of carbon, sulfur, oxygen and nitrogen. Applicants respectfully assert that claim 11 is not indefinite in view of the amendments to claims 10 and 11. Further, Applicants respectfully submit that at least paragraphs [0027] and [0028] of the instant specification render claim 11 definite. For example, paragraph [0027] recites "carbon nanotubes functionalized with a species having nucleation sites operable for polymerization (such as species having carbon, sulfur, oxygen, and nitrogen sites for polymerization)". Paragraph [0028] recites "[treatment] with a deprotonation agent to deprotonate the nucleation sites to form initiator groups for polymerization." In further view of the specific examples presented at the end of paragraph [0027], Applicants respectfully assert that claim 11 is not indefinite, since one of ordinary skill in the art would recognize the invention described by the nucleation sites in claim 11.

In view of the foregoing remarks and amendments, Applicants respectfully request that the Examiner's rejection of claim 11 under 35 U.S.C. § 112, second paragraph, be withdrawn.

I.2.   Rejection of Claim 12

The Examiner asserts that the recitation of NHBoc in claim 12 is considered indefinite. The Examiner questions 'What is Boc?'. Applicants respectfully traverse the rejection of this claim under 35 U.S.C. § 112, second paragraph, for at least the reasons set forth below.

Applicants respectfully assert that the term Boc (also referred to as BOC or t-BOC) is well known in the art of synthetic organic chemistry and one of ordinary skill in the art would readily understand that which is being recited in claim 12. Boc represents a shorthand notation for a *t*-butoxycarbonyl group, which is commonly used as a protecting group for amino compounds. The Examiner is referred to http://en.wikipedia.org/wiki/Di-tert-butyl_dicarbonate for a general discussion of BOC compounds, which presents evidence that this term is considered well known to those of ordinary skill in the art.

As further evidence that Boc is synonymous with a *t*-butoxycarbonyl group and well known to those of ordinary skill in the art, Applicants also present the reference S.D. Tarbell, *et al.*, "New Method to Prepare N-t-Butoxycarbonyl Derivatives and the Corresponding Sulfur Analogs from di-t-Butyl Bicarbonate or di-t-Butyl Dithiol Dicarbonates and Amino Acids", *Proc. Natl. Acad. Sci.*, 69 (1972), pp. 730-732 as Appendix I of this response (see Pages A1 – A3). In particular, Applicants call the Examiner's attention to the Abstract of this publication, where it is taught that the term *t*-butoxycarbonyl is synonymous with the term *t*-BOC. Therefore, Applicants respectfully assert that claim 12 is not indefinite, since one of ordinary skill in the art would recognize the invention described by CNT-C_6H_4-NHBoc in claim 12.

In view of the foregoing remarks, Applicants respectfully request that the Examiner's rejection of claim 12 under 35 U.S.C. § 112, second paragraph, be withdrawn.

I.3.   Rejection of Claim 29

The Examiner asserts that the recitation of 'average chain length' in claim 29 is considered indefinite. In the interest of expediting prosecution, Applicants have cancelled claim 29 and depending claim 30, rendering this rejection moot.

I.4.   Rejection of Claim 32

The Examiner asserts that claim 32 is indefinite for the recitation of 'TiCl$_4$'. The Examiner asserts that there is inadequate antecedent basis from the previous for this feature. Applicants respectfully traverse the rejection of this claim under 35 U.S.C. § 112, second paragraph, for at least the reasons set forth below.

Applicants presume that the Examiner requires clarification of how the catalyst comprising TiCl$_4$ is germane to the initiating step of an anionic or ring opening polymerization. Applicants respectfully assert that one of ordinary skill in the art would recognize that catalysts comprising TiCl$_4$ are well known in the polymerization arts, particularly in Ziegler-Natta catalysts for alkene polymerization. The Examiner is referred to http://en.wikipedia.org/wiki/Ziegler-Natta_catalyst for a general discussion of Ziegler-Natta catalysts and TiCl$_4$ as a component of Ziegler-Natta catalysts.

Applicants also submit supplemental references in Appendices II and III of this response, which show that catalysts comprising TiCl$_4$ are well known in the art of anionic polymerization and ring opening polymerization. In support of anionic polymerization, Applicants submit the reference N. Ashikari, *et al.*, "Polymerization of Propylene with Tin Tetraalkyl-Titanium Tetrachloride Catalyst", *Bull. Chem. Soc. Japan*, 34 (1961), pp. 767-770 as Appendix II of this response (see pages A4 – A7). Applicants particularly call the Examiner's attention to the first paragraph of the Discussion section (p. 770), which teaches that Ziegler catalysts give a cationic or <u>anionic reaction</u> depending on the catalyst composition. In support of ring opening polymerization, Applicants submit a portion of United States Patent 5,034,482 (hereinafter, *Kohara*), issued July 23, 1991, as Appendix III of this response (see pages A8 – A11). Support that Ziegler-type catalysts comprising TiCl$_4$ find utility in ring opening polymerization may be found in *Kohara* in at least the Abstract; Column 2, lines 16 – 29; Column 3, lines 60 – 62; and Column 5, lines 11 – 16. Applicants respectfully submit that these references in combination provide sufficient evidence that TiCl$_4$ is germane to the art of anionic polymerization and ring-opening polymerization and is well known to those of ordinary skill in the art. Therefore, Applicants respectfully assert that claim 32 is not indefinite, since TiCl$_4$ is germane to anionic polymerization and ring opening polymerization and thus has proper antecedent support.

In view of the foregoing remarks, Applicants respectfully request that the Examiner's rejection of claim 32 under 35 U.S.C. § 112, second paragraph, be withdrawn.

II.　Claim Rejections Under 35 U.S.C. § 103

Claims 1 – 34 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over WO 02/060812 (herinafter, *Tour*) in view of United States Patent 3,554,992 (hereinafter, *Lamb*). Office Action item 5. Applicants respectfully traverse the rejection of these claims.

Standard of Review

The standard of review for obviousness is set forth as follows. "To establish *prima facie* obviousness of a claimed invention, all features must be taught or suggested by the prior art." *In re Royka,* 490 F.2d 981, 180 U.S.P.Q. 580 (C.C.P.A. 1974). Furthermore, "[r]ejections on obviousness grounds cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness". *KSR Int'l Co. v. Teleflex Inc.,* 127 S.Ct. 1727, 1741 (2007) citing with approval *In re Kahn,* 441 F.3d 977, 988 (Fed. Cir. 2006). In addition, in issuing rejections under 35 U.S.C. § 103(a), the Examiner must consider an invention and the prior art as a whole in accordance with the requisite *Graham* factual inquiries. MPEP § 2141; *Ruiz v. A.B. Chance Co.* 69 U.S.P.Q.2d 1686, 1690 (Fed. Cir. 2004).

Assertions by the Examiner

With regard to claims 1, 2, 3 and 10, the Examiner asserts that *Tour* teaches SWNTs functionalized with an aryl chlorine-containing functionality. The Examiner also asserts that *Tour* teaches that halogenated SWNTs can participate in reactions with alkyl-lithium reagents via a Grignard reaction mechanism. The Examiner also asserts that *Tour* teaches that functionalized SWNTs can undergo polymerization, including anionic polymerization (claims 125 – 129 of *Tour*). The Examiner asserts that the feature 'operable for anionic or ring opening polymerization' recited in claim 10 is inherently possessed in *Tour*. With regard to claims 33 and 34, the Examiner asserts that unless the recited intended uses result in a structural difference between the claimed invention and the prior art, then the prior art meets the claim if the prior art structures are capable of performing the intended use.

Although *Tour* does not teach the specific mechanism for preparing a polymer, the Examiner asserts that *Lamb* teaches using a Grignard reaction for initiating a polymerization process. The Examiner asserts that *Lamb* teaches specific types of monomers and various hydrocarbon and ethereal solvents for the polymerization process, including THF. The Examiner asserts that the precipitating method taught by *Lamb* would be recognized by one of ordinary skill in the art to be functionally equivalent to the terminating agents of claims 25 and 26. The Examiner asserts that the concentration and temperature variation of claims 26 and 27 are considered obvious since they apply to routine optimization. In view of the foregoing, the Examiner asserts that one of ordinary skill in the art would have been motivated to incorporate the specifics taught by *Lamb* into the teachings of *Tour* to obtain the claimed invention.

Regarding the 'deprotonating agent' of claims 14 and 15, the Examiner repeats the assertion that asserts that *Tour* teaches that halogenated SWNTs can participate in reactions with an alkyl-lithium reagent via a Grignard reaction mechanism. The Examiner also repeats the assertion that *Tour* teaches that functionalized SWNTs can undergo various polymerizations, including anionic polymerization. The Examiner asserts that the minor variation of reaction conditions in claims 27 and 28 is considered obvious, in view of the expectation of success of developing a polymerization process using halogenated SWNTs.

Applicant's Characterization of Tour and Lamb

Applicants respectfully assert that the Examiner has mischaracterized the teachings of both *Tour* and *Lamb,* and in doing so has failed to demonstrate a *prima facie* case of obviousness of Applicants' claims.

Applicants respectfully traverse the Examiner's position that *Tour* teaches a reaction of halogenated SWNTs with an alkyl-lithium reagent via a Grignard reaction mechanism. Applicants respectfully assert that *Tour* teaches a reaction of fluorinated nanotubes with strong nucleophiles, such as alkyl lithium reagents (see *Tour*, page 2, lines 13 – 14). As such, Applicants respectfully assert that the reaction taught by *Tour* is a nucleophilic substitution reaction in which fluorine is displaced by a strong nucleophile, the alkyl lithium reagent. Evidence to this effect may be found in United States Patent 6,827,918, issued December 7, 2004, (hereinafter, *Margrave*), a portion of which is included as Appendix IV of this response

(see pages A12 – A16). The reaction of fluorinated carbon nanotubes with an alkyl lithium species is taught by *Margrave* to be a nucleophilic substitution reaction in at least the Abstract; Column 4, lines 1 – 18; Column 14, lines 51 – 66, and Column 17, line 58 through Column 19, line 6.

Applicants respectfully traverse the Examiner's position that *Lamb* teaches using a Grignard reaction for initiating a polymerization process. Applicants respectfully assert that *Lamb* teaches using a Grignard complex mounted on a solid support, which has a formula RXMg(hal) (see *Lamb*, Column 2, lines 1 – 6). *Lamb* specifically teaches that the Grignard complex is formed by the reaction of a Grignard reagent (R'Mg(hal)) with an olefinic oxide or compound containing an unsaturated linkage (see *Lamb*, Column 2, lines 8 – 15). For example, *Lamb* teaches reactions of Grignard reagents with nitriles, nitroso compounds, aldehydes, ketones, esters, inorganic compounds and olefinic oxides to form the Grignard complex (see *Lamb*, column 2, lines 25 – 66). Applicants respectfully assert that the Grignard complex taught by *Lamb* is no longer an organometallic compound containing a carbon-metal bond, but is instead a simple salt containing a magnesium cation and an anion of an organic addition product. Therefore, Applicants respectfully assert that *Lamb* does not teach a Grignard reaction for initiating a polymerization reaction as asserted by the Examiner.

Applicants provide a reference from Morrison, *et al.*, "Organic Chemistry", 5th edition, Boston: Allyn & Bacon, Inc., 1987, p. 655 as Appendix V of this response (see page A-17) attesting to the fact that the Grignard complex taught by *Lamb* is a simple salt. For example, *Lamb* teaches that Grignard complexes are formed by a reaction between a Grignard reagent and aldehydes or ketones (see *Lamb*, column 2, lines 39 – 49). Section 17.15 of the reference presented in Appendix V clearly shows that the product of a reaction between a Grignard reagent and an aldehyde or ketone is a simple salt containing a magnesium cation and an oxygen anion. Similar simple salts are formed in the formation of the other Grignard complexes taught in *Lamb*.

In summary, *Tour* teaches a nucleophilic substitution reaction of fluorinated carbon nanotubes with alkyllithium reagents to form alkylated carbon nanotubes. There is no formation of a polymerizable species such as an aryl-lithium species, an aryl-metal species or a deprotonated species in this reaction. Likewise, *Tour* does not teach using an aryl-lithium

species, an aryl-metal species or a deprotoned species in anionic or ring-opening polymerization. Further, *Lamb* does not teach a Grignard reaction for initiating a polymerization process, since *Lamb* reacts a Grignard reagent with an olefinic oxide or compound containing an unsaturated linkage to form a Grignard complex. After the reaction to form the Grignard complex in *Lamb*, there is no longer organometallic compound having a carbon-metal bond available to initiate polymerization.

Independent Claim 1 is Not Obvious

Applicants respectfully assert that independent claim 1, as amended, is not obvious, since *Tour* and *Lamb* fail to teach or suggest all features of this claim as is required to establish obviousness. As amended, step c) of claim 1 recites that 'at least one reagent reacts with the functionalized carbon nanotubes to form a polymerizable species'. Further, step c) of claim 1 requires that the polymerizable species is selected from the group consisting of an aryl-lithium species, an aryl-metal species, and initiator groups. In addition, step c) of claim 1 requires that the initiator groups are formed by deprotonation of nucleation sites on the functionalized carbon nanotubes.

As discussed hereinabove, Applicants respectfully assert that *Tour* does not teach or suggest the reaction of at least one reagent with functionalized carbon nanotubes to form a polymerizable species, as required by claim 1, since *Tour* teaches a nucleophilic substitution reaction of fluorinated carbon nanotubes with an alkyllithium reagent. The nucleophilic substitution reaction of *Tour* is not germane to a polymerizable species selected from the group consisting of aryl-lithium species, aryl-metal species and initiator groups, as is now required by Applicants' claim 1. Although claims 125 – 129 of *Tour* reference anionic and ring-opening polymerization, *Tour* does not teach or suggest adding any of the reagents in claim 1 steps c)(i), c)(ii) or c)(iii) to form a polymerizable species. Hence, *Tour* does not teach or suggest a reaction between a monomer and a polymerizable species, wherein the polymerizable species is selected from the group consisting of an aryl-lithium species, an aryl-metal species and initiator groups.

Furthermore, Applicants respectfully assert that since *Lamb* does not teach or suggest use of a Grignard reagent in anionic polymerization, *Lamb* cannot teach or suggest a Grignard reaction for initiating a polymerization process, as is asserted by the Examiner. Accordingly,

Applicants respectfully assert that there is no motivation to combine *Lamb* with *Tour*, since the species for initiating polymerization are not the same. The standard of review for establishing a motivation to combine references is set forth as follows:

> "A rationale to support a conclusion that a claim would have been obvious is that all the claimed elements were known in the prior art and one skilled in the art could have combined the elements as claimed by known methods with no change in their respective functions, and the combination would have yielded nothing more than predictable results to one of ordinary skill in the art." M.P.E.P. § 2143.02. Although "[o]bviousness does not require absolute predictability...at least some degree of predictability is required." *Ibid.*

In the instant case, since *Lamb* teaches the use of a Grignard complex (a simple salt) for catalyzing a polymerization reaction, there is no motivation to combine *Lamb* with *Tour* since there would be no way for one of ordinary skill in the art would to predict that the Grignard complex of *Lamb* would react with the functionalized carbon nanotubes of *Tour*. In fact, Applicants respectfully assert that the Examiner's suggestion to combine *Lamb* with *Tour* would instead result in a combination that would be inoperative for the polymerization reaction of claim 1.

In summary, *Tour* and *Lamb* do not teach or suggest all of the limitations of Applicants' claim 1, as this claim presently stands amended. Furthermore, there is no motivation to combine *Lamb* with *Tour*. Hence, Applicants respectfully assert that claim 1 is not obvious under 35 U.S.C. § 103(a). Applicants therefore respectfully request that the Examiner's rejection of claim 1 under 35 U.S.C. § 103(a) be withdrawn.

Independent Claim 2 is Not Obvious

Applicants respectfully assert that independent claim 2, as amended, is also not obvious, since *Tour* and *Lamb* fail to teach or suggest all features of this claim as is required to establish obviousness. As amended, step c) of claim 2 recites that 'the alkyllithium species reacts with the aryl halide functionalized carbon nanotubes to form an aryl-lithium species comprising aryl-lithium bonds'. Further, step e) of claim 2 recites that the polymerization reaction occurs between the monomer and the aryl-lithium species.

As discussed hereinabove, Applicants respectfully assert that *Tour* does not teach or

suggest an aryl-lithium species or a polymerization reaction between a monomer and an aryl-lithium species, as required by claim 2, since *Tour* teaches a nucleophilic substitution reaction of fluorinated carbon nanotubes with an alkyllithium reagent. Therefore, the nucleophilic substitution reaction of *Tour* is not germane to formation of an aryl-lithium species, as is now required by Applicants' claim 2. Although claims 125 – 129 of *Tour* reference anionic and ring-opening polymerization, *Tour* does not teach or suggest adding an alkyllithium species to functionalized carbon nanotubes to form an aryl-lithium species for initiating a polymerization reaction.

Applicants respectfully assert that since *Lamb* does not teach or suggest use of a <u>Grignard reagent</u> in anionic polymerization, *Lamb* does not teach or suggest a Grignard reaction for initiating a polymerization process, as is asserted by the Examiner. Accordingly, Applicants respectfully assert that there is no motivation to combine *Lamb* with *Tour*, since the <u>Grignard complexes</u> taught by *Lamb* are not germane to formation of the aryl-lithium species recited in Applicants' claim 2, and the species for initiating polymerization are not the same. Applicants respectfully assert that there would be no way for one of ordinary skill in the art to predict that the <u>Grignard complex</u> of *Lamb* would react with the functionalized carbon nanotubes of *Tour*. In fact, Applicants respectfully assert that the Examiner's suggestion to combine *Lamb* with *Tour* would instead result in a combination that would be inoperative for the polymerization reaction of claim 2.

In summary, *Tour* and *Lamb* do not teach or suggest all of the limitations of Applicants' claim 2, as this claim presently stands amended. Furthermore, there is no motivation to combine *Lamb* with *Tour*. Hence, Applicants respectfully assert that claim 2 is not obvious under 35 U.S.C. § 103(a). Applicants therefore respectfully request that the Examiner's rejection of claim 2 under 35 U.S.C. § 103(a) be withdrawn.

Independent Claim 3 is Not Obvious

Applicants respectfully assert that independent claim 3, as amended, is also not obvious, since *Tour* and *Lamb* fail to teach or suggest all features of this claim as is required to establish obviousness. As amended, step c) of claim 3 recites that 'the metal reacts with the aryl halide functionalized carbon nanotubes to form an aryl-metal species comprising aryl-metal bonds'.

Step e) of claim 3 recites that the polymerization reaction occurs between the monomer and the aryl-metal species.

As discussed hereinabove, Applicants respectfully assert that *Tour* does not teach or suggest an aryl-metal species or a polymerization reaction between a monomer and an aryl-metal species, as required by claim 3, since *Tour* teaches a nucleophilic substitution reaction of fluorinated carbon nanotubes with an alkyllithium reagent. Therefore, the nucleophilic substitution reaction of *Tour* is not germane to formation of an aryl-metal species comprising aryl-metal bonds, as is required by Applicants' claim 3. Although claims 125 – 129 of *Tour* reference anionic and ring-opening polymerization, *Tour* does not teach or suggest adding a metal to form an aryl-metal species having aryl-metal bonds for initiating a polymerization reaction.

Applicants respectfully assert that since *Lamb* does not teach or suggest use of a Grignard reagent in anionic polymerization, *Lamb* does not teach or suggest a Grignard reaction for initiating a polymerization process, as is asserted by the Examiner. Accordingly, Applicants respectfully assert that there is no motivation to combine *Lamb* with *Tour*, since the Grignard complexes taught by *Lamb* are not germane to formation of the aryl-metal species recited in Applicants' claim 3, and the species for initiating polymerization are not the same. Applicants respectfully assert that there would be no way for one of ordinary skill in the art to predict that the Grignard complex would react with the functionalized carbon nanotubes of *Tour*. In fact, Applicants respectfully assert that the Examiner's suggestion to combine *Lamb* with *Tour* would instead result in a combination that would be inoperative for the polymerization reaction of claim 3.

In summary, *Tour* and *Lamb* do not teach or suggest all of the limitations of Applicants' claim 3, as this claim presently stands amended. Furthermore, there is no motivation to combine *Lamb* with *Tour*. Hence, Applicants respectfully assert that claim 3 is not obvious under 35 U.S.C. § 103(a). Applicants therefore respectfully request that the Examiner's rejection of claim 3 under 35 U.S.C. § 103(a) be withdrawn.

Independent Claim 10 is Not Obvious

Applicants respectfully assert that independent claim 10, as amended, is also not obvious, since *Tour* and *Lamb* fail to teach or suggest all features of this claim as is required to establish obviousness. As amended, step c) of claim 10 recites 'adding a deprotonating agent to the solvent, wherein the deprotonating agent deprotonates the nucleation sites to form initiator groups'. Step e) of claim 10 recites that that polymerization reaction occurs between the monomer and the initiator groups.

As discussed hereinabove, Applicants respectfully assert that *Tour* does not teach or suggest a deprotonating agent, deprotonation of nucleation sites to form initiator groups or a polymerization reaction between a monomer and initiator groups, as required by claim 10, since *Tour* teaches a nucleophilic substitution reaction of fluorinated carbon nanotubes with an alkyllithium reagent. Therefore, the nucleophilic substitution reaction of *Tour* is not germane to formation of an initiator group, as is required by Applicants' claim 10. Hence, initiator groups are neither taught, either expressly or inherently, in *Tour*. Although claims 125 – 129 of *Tour* reference anionic and ring-opening polymerization, *Tour* does not teach or suggest deprotonation of nucleation sites of functionalized carbon nanotubes to form initiator groups for initiating a polymerization reaction.

Applicants respectfully assert that since *Lamb* does not teach or suggest use of a <u>Grignard reagent</u> in anionic polymerization, *Lamb* does not teach or suggest a Grignard reaction for initiating a polymerization process, as is asserted by the Examiner. Accordingly, Applicants respectfully assert that there is no motivation to combine *Lamb* with *Tour*, since the <u>Grignard complexes</u> taught by *Lamb* are not germane to formation of the initiator groups recited in Applicants' claim 10. Specifically, Applicants' claim 10 requires a deprotonation in step c). *Lamb* expressly requires an addition reaction of a Grignard reagent to an olefinic oxide or compound containing an unsaturated linkage to form a <u>Grignard complex</u>. Since *Lamb* expressly requires an addition reaction of the Grignard reagent, it is inherent that *Lamb* cannot teach deprotonation, since an initiator group is merely a deprotonated nucleation site. In other words, since *Lamb* requires an addition reaction, *Lamb* does not teach a simple deprotonation to form an initiator group, as a new group is formed as a result of the addition reaction. Further, *Lamb* does

not teach or suggest a polymerization reaction between a monomer and an initiator group as is required by step e) of claim 10, since *Lamb* inherently does not teach initiator groups.

In summary, *Tour* and *Lamb* do not teach or suggest all of the limitations of Applicants' claim 10, as this claim presently stands amended. Furthermore, there is no motivation to combine *Lamb* with *Tour*. Hence, Applicants respectfully assert that claim 10 is not obvious under 35 U.S.C. § 103(a). Applicants therefore respectfully request that the Examiner's rejection of claim 10 under 35 U.S.C. § 103(a) be withdrawn.

Dependent Claims 4 – 9, 11 – 29 and 32 – 34 are Not Obvious

Applicants respectfully assert that independent claims 1 – 3 and 10 are allowable in view of the remarks and amendments presented hereinabove. Claims 4 – 9, 11 – 29 and 32 – 34 depend either directly or indirectly from allowable claims 1 – 3 and 10 and are patentable for at least the same reasons. *In re Fine,* 837 F.2d 1071, 5 U.S.PQ.2d 1596 (Fed. Cir. 1988). Therefore, Applicants respectfully request that the Examiner's rejection of dependent claims 4 – 9, 11 – 29 and 32 – 34 under 35 U.S.C. § 103(a) be withdrawn.

CONCLUSIONS

Claims 1 – 28 and 31 – 34 remain pending in the application. Applicants respectfully submit that claims 1 – 28 and 31 – 34, as these claims presently stand amended, are in a condition for allowance based on the remarks presented hereinabove.

If additional fees are due and are not included, the Director is hereby authorized to charge any fees or credit any overpayment to Deposit Account Number 23-2426 of Winstead PC (referencing matter 11321-P068WOUS).

If the Examiner has any questions or comments concerning this paper or the present application in general, the Examiner is invited to call the undersigned at 713-650-2782.

Respectfully submitted,

WINSTEAD PC

Attorney/Agents for Applicant

Date: <u>March 16, 2009</u>

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APPENDIX I

New Method to Prepare N-t-Butoxycarbonyl Derivatives and the Corresponding Sulfur Analogs from di-t-Butyl Dicarbonate or di-t-Butyl Dithiol Dicarbonates and Amino Acids

(blocking groups/peptide synthesis)

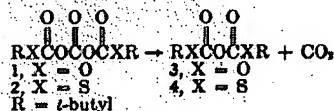D. STANLEY TARBELL, YUTAKA YAMAMOTO, AND BARRY M. POPE

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37203

ABSTRACT   Di-t-butyl dicarbonate and one of its dithiol analogs, practical methods of preparation for which are given, react with amino-acid esters to form the N-t-butoxycarbonyl (t-BOC) derivatives and the thiol analogs in good yield under mild conditions. The thiol analogs are stable to acidic conditions, which rapidly remove the t-BOC group itself. t-Butyl trimethylsilyl carbonate forms a $(CH_3)_3Si$ ether from a N-thiol-t-BOC serine methyl ester. The N-thiol-t-BOC group can be removed from the —NHCOSR (R = t-butyl) by heating with peroxide–acetic acid.
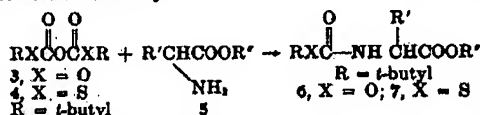
Action of the dicarbonates described above has not been attended by racemization in the cases examined. The two dicarbonates may be useful as agents for selective blocking and deblocking of amino or other groups.

Recent studies (1, 2) in this laboratory have made the tricarbonates 1 and 2 readily available. From them, without isolation of the tricarbonates if desired, the corresponding *dicarbonates* 3 and 4 are readily prepared by treatment with tertiary amines or by mild heating (3).

$$\underset{\substack{1,\ X = O \\ 2,\ X = S \\ R = t\text{-butyl}}}{RXCOCOCXR} \rightarrow \underset{\substack{3,\ X = O \\ 4,\ X = S}}{RXCOCXR} + CO_2$$

The ready availability of the sulfur and oxygen dicarbonates (for nomenclature, see ref. 2.) suggested that their behavior with α-amino acids should be studied, because the expected reaction (4, 5) would lead to the t-butoxycarbonyl (t-BOC) derivatives, or their sulfur analogs (thiol-t-BOC); the t-BOC group is a standard protecting group for the amino group in peptide syntheses. The reaction of 3 and 4 should allow synthesis of such derivatives under mild conditions, and might have useful applications in selective alteration of enzymes or proteins.

The expected reaction (4, 5) took place readily; the amino-acid ester hydrochloride was usually used, neutralized with bicarbonate, and heated briefly in tetrahydrofuran (THF) or chloroform to give the product in good yield. Free glycine was also used successfully.
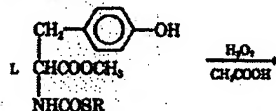
$$\underset{\substack{3,\ X = O \\ 4,\ X = S \\ R = t\text{-butyl}}}{RXCOCXR} + \underset{\substack{\\ \\ NH_2 \\ 5}}{R'CHCOOR'} \rightarrow \underset{\substack{\\ R = t\text{-butyl} \\ 6,\ X = O;\ 7,\ X = S}}{RXC-NH\ CHCOOR'}$$

Some of the derivatives prepared in model studies are shown in Table 1.

The advantage of the t-BOC group in peptide syntheses lies in its rapid removal, by mild acid, presumably via alkyl–
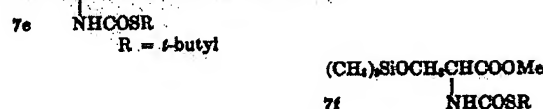
oxygen cleavage and a carbonium ion mechanism. The thiol analogs 7, however, as would be predicted from much work in this and other laboratories (see ref 1 for references), are stable to acid conditions, such as formic acid or CF_3COOH, that cleave the t-BOC group completely. The thiol analog 7 can be cleaved by Kollonitsch's (6) method with peracids, without racemization.

$$\underset{\substack{L \\ \\ NHCOSR}}{\overset{\substack{CH_2 \\ |}}{CHCOOCH_3}} \longrightarrow \overset{\substack{H_2O_2 \\ CH_3COOH}}{\longrightarrow}$$

L-Tyr methyl ester, of unchanged rotation.

This difference in rate of cleavage by acid between the oxygen and sulfur analogs 6 and 7 might allow preferential deblocking of amino groups in complex molecules.

The yield of isolated material in Table 1 was usually high, although some of the t-BOC derivatives 6 (as esters) were difficult to purify. With 1 mol of dicarbonate, no diacylated material was obtained from serine or tyrosine. The trimethylsilyl ether of the serine thiol derivative was prepared as below (7).

$$\underset{\substack{7e \\ NHCOSR}}{HOCH_2CHCOOMe} + ROCOOSi(CH_3)_3 \rightarrow$$

$$R = t\text{-butyl}$$

$$\underset{\substack{7f \\ NHCOSR}}{(CH_3)_3SiOCH_2CHCOOMe}$$

Tests of acidic hydrolysis of N-t-BOC methyl ester of Tyr showed no appreciable racemization during the process.

It is well known that the diethyl analog 8 of 3, usually called diethyl pyrocarbonate, reacts with various enzymes, proteins (8), and with adenosine and adenine (9). Whether

$$\underset{\substack{\\ ROCOCOR}}{\overset{O\ \ O}{\parallel\ \ \parallel}} \qquad 8,\ R = Et.$$

differences in reactivity of 8, 3, and 4 with amino or other nucleophilic groups and differences in their relative rates of removal will make these t-butyl dicarbonates 3 and 4 useful reagents remains to be seen.

We have also made the mixed oxygen–sulfur dicarbonate 9; its reactions with nucleophiles are being investigated.

$$\underset{\substack{\\ RSCOCOR}}{\overset{O\ \ O}{\parallel\ \ \parallel}} \qquad 9,\ R = t\text{-butyl}$$

Modified procedure for preparation of di-t-butyl tricarbonate (1) and di-t-butyl dicarbonate (3) ref. 1

Potassium t-butoxide (44.8 g, 0.4 mol) was dissolved in 550 ml of freshly distilled THF at room temperature. Dry CO_2

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was passed through the solution, which was cooled with an ice-salt bath (−15 to about −20°) with vigorous stirring for 30 min. A solution of about 20 ml of phosgene in 85 ml of benzene was added dropwise. The reaction mixture was stirred for an additional hour, while the bath temperature was maintained at −15° to about −20°. Dry nitrogen was bubbled into the cold solution for 45 min.

The resulting solution was evaporated to about 100 ml in a rotary evaporator under reduced pressure by a rotary pump, while being kept below 0°.

The precipitate was removed by suction filtration through a fritted-glass filter funnel of medium porosity, which had previously been cooled with ice-cold pentane. The precipitate was washed with pentane and the solution was completely evaporated at a temperature below 0° in a rotary evaporator under reduced pressure by a rotary pump to give 33.7 g (64.1%) of colorless fine solid of 1.

In 75 ml of CCl_4, 20 g of unrecrystallized tricarbonate was dissolved, and 0.1 g of freshly sublimed 1,4-diazobicyclo-[2.2.2]octane (Dabco) was added. This mixture was stirred at room temperature for 45 min, then the solvent was evaporated by a rotary evaporator.

After the Dabco was removed by sublimation, the solution was distilled to give 14.8 g (89%) of di-*t*-butyl dicarbonate, bp 50–51° (0.3 mm), whose spectroscopic properties agreed with reported values (1).

Modified procedure for preparation of di-*t*-butyl dithiol dicarbonate (4) via di-*t*-butyl dithiol tricarbonate (2)

Sodium hydride (6 g, in 50% mineral oil dispersion) was washed with three 50-ml portions of THF and suspended in 250 ml of THF. A solution of 9 g of *t*-butyl mercaptan in 30 ml of the same solvent was added dropwise with stirring; the resulting mixture was refluxed for 1 hr and cooled with an ice-salt bath (−15° to about −20°). Dry carbon dioxide was passed into the mixture for 30 min with vigorous stirring. A solution of about 9 g of phosgene in 25 ml of benzene was added dropwise. The reaction mixture was stirred for an additional 30 min, while the bath temperature was maintained at −15° to about −20°. The NaCl was removed by filtration as before, the filtrate and washings were completely removed by evaporation with an oil pump, and the resulting oily tricarbonate was heated at a bath temperature of 85–90° until evolution of CO_2 ceased. Distillation gave 8.9 g (71%, overall, from the mercaptan) of material, bp 82–83° (0.5 mm) with the spectroscopic properties previously reported for the dithiol dicarbonate 4.

N-*t*-BOC glycine ethyl ester (6a)

A typical preparation of compounds in Table 1A follows. Glycine ethyl ester hydrochloride (1.395 g, 0.01 mol) was suspended in 20 ml of chloroform, and 0.84 g (0.01 mol) of Na-HCO₃ in 15 ml of H_2O was added. Sodium chloride (2 g) was added, and then 2.18 g (0.01 mol) of di-*t*-butyl dicarbonate 3 dissolved in a few milliliters of $CHCl_3$; the mixture was refluxed for 90 min. After the solution cooled, it was separated, and the aqueous layer was extracted with $CHCl_3$; the $CHCl_3$ solution was dried and evaporated at room temperature. The colorless product was then distilled at 104–105° (0.15 mm), to give 1.8 g (89%) of *N*-*t*-butoxycarbonyl glycine ethyl ester (6a). The IR spectrum (CCl_4) showed -NH stretch at 3440 cm⁻¹ and carbonyl bands at 1725 and 1745. The NMR spectrum

(CCl_4) in ppm: 1.27 (t, 3H); 1.45 (s, 9H); 3.8 (d, 2H); 4.17 (q, 2H); 5.67 (t, 1H), in satisfactory agreement with the reported values (ref. *e*, Table 1).

As an example of other analytical data for Table 1A, *N*-*t*-BOC L-serine methyl ester (6c) may be quoted. It showed IR (CCl_4) 3300–3550 (OH and NH), 1750 and 1730 (C=O), and NMR (CCl_4) at 1.43 (s, 9H); 3.73 (s, 3H); 3.8–4.4 (m, 4H) and 5.9 (d, 1H). *Anal.* Calcd. for $C_9H_{17}NO_5$: C, 49.30; H, 7.82: Found: C, 49.15; H, 8.00.

Action of trifluoroacetic acid −H_2O on *N*-*t*-BOC tyrosine methyl ester (6f)

The *N*-*t*-BOC compound 6f (0.3023 g) was allowed to stand in a mixture of 15 ml of CF_3COOH and 5 ml of H_2O for 15 min at room temperature; the solution was then evaporated, neutralised with 3% NH_4OH, saturated with NaCl, and extracted with $CHCl_3$. The $CHCl_3$ layer was dried and evaporated under reduced pressure to give 0.1995 g (82.8%) of white solid. The solid was recrystallized from ethyl acetate and has a mp of 134–135°C; it showed no depression of melting point in a mixture melting point with authentic L-tyrosine methyl ester. The $[\alpha]^{25}_D$ for the tyrosine methyl ester recovered from the *N*-*t*-BOC derivative, as above, was +26.9° (*C* = 2.36, CH_3OH); the starting material, before treatment with the dicarbonate, showed $[\alpha]^{25}_D$ + 26.5° (*C* = 2.33, CH_3OH).

N-Thiol-*t*-BOC L-tyrosine methyl ester (7c). Method A

To a solution of 2.5 g (0.01 mol) of di-*t*-butyl dithiol dicarbonate in 10 ml of THF was added a solution of 1.95 g (0.01 mol) of L-tyrosine methyl ester in the same solvent with stirring at room temperature. L-Tyrosine ester gradually reacted, evolution of gas was observed, and the reaction mixture was refluxed for 30 min. Removal of solvent under reduced pressure gave a viscous oil, which was crystallized by washing with petroleum ether. Recrystallisation from benzene (about 25 ml of benzene solution was concentrated to about 10 ml) gave 2.4 g of colorless crystals, mp 110–112°C. Concentration of the mother liquors and addition of cyclohexane yielded 0.4 g more of the same crystals; total amount of crystals was 2.8 g (90%). The properties were IR (CCl_4); 1745, 1670 cm⁻¹; NMR (CCl_4) 1.50 (*t*-butyl protons). *Anal.* Calcd. for $C_{15}H_{21}NO_4S$: C, 57.86; H, 6.80. Found: C, 57.97; H, 6.71.

N-thiol-*t*-BOC L-serine methyl ester (7e). Method B

L-Serine methyl ester hydrochloride (1.55 g) was dissolved in H_2O containing 1 eq of $NaHCO_3$. Di-*t*-butyl dithiol dicarbonate (2.5 g), and enough alcohol to form a homogeneous solution, were added. The reaction was kept at room temperature for several hours and concentrated under reduced pressure. The resulting solution was saturated with NaCl, and extracted with $CHCl_3$, the $CHCl_3$ layer was dried, and solvent was evaporated under reduced pressure. The viscous liquid obtained had reasonable IR and NMR spectra for structure 6c, but decomposed on attempted distillation, apparently to form a 2-oxooxazolidine with loss of $(CH_3)_3CSH$.

The crude 7e (1.7 g) was silylated to the *O*-trimethylsilyl compound 7f by heating at 95–100°C (bath temperature) for 16 hr with stirring with 4.5 g of *t*-butyl trimethylsilyl carbonate (7). The reaction mixture was evaporated with an aspirator. Distillation gave 1.6 g of the *O*-silylated compound 7f, [71%, bp 112–113°C (0.35 mm)]. The properties were IR

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732   Chemistry: Tarbell *et al.*   *Proc. Nat. Acad. Sci. USA 69 (1972)*

TABLE 1.

$$\text{A.}\quad \text{RO}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{NH—}\overset{\text{R}'}{\overset{|}{\text{CH}}}\text{COOR}'.\ \text{Prepared from the Dicarbonate 3.}$$
R = *t*-butyl

Compound	Amino acid	R″	Characterization*	mp (solvent) or bp (mm)
6a	Gly	Et	a, b, e, known	104–105 (0.15)
6b	D-Try	Et	a, b, c, g	166–168 (CHCl₃)
6c	L-Ser	Me	a, b, c	126 (0.35)
6d	L-Leu	Et	a, b, c	97 (0.2)
6e	L-Pro	C₆H₅CH₂	a, b, c	136 (0.35)
6f	L-Tyr	Me	a, b, d, f, known	105–106 (C₆H₁₂)
6g	4-OH-L-Pro	Et	a, b, c	142 (0.35)
6h	L-Ala	Me	a, b, c	60 (0.03)

$$\text{B.}\quad \text{RS}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{NH}\overset{\text{R}'}{\overset{|}{\text{CH}}}\text{COOR}'.\ \text{Prepared from the Dicarbonate 4.}$$
R = *t*-butyl

No.	Amino acid	R″	Characterization	mp (solvent) or bp (mm)	Method
7a	Gly	H	a, b, c	129–130 (CHCl₃)	B
7b	Gly	Et	a, b, c	113–114 (1.1)	A
7c	L-Tyr	Me	a, b, c, d, no O-acylation	110–112 (C₆H₆)	A
7d	L-His	Me	a, b, c, N-α, N-im derivative	98–99.5 (EtOH–H₂O)	B
7e	L-Ser	Me	Purified through silyl derivative	—	
7f	(CH₃)₃SiOCH₂CHCOOH	Me	a, b, c	112–113 (0.35)	
	$\quad$ NH₂				

* (a) Correct NMR spectrum; (b) correct IR spectrum; (c) correct elemental analysis; (d) hydrolysis to L-Tyr methyl ester; (e) spectra (IR and NMR) agree with those of Tarbell, D. S. & Insalaco, M. A. (1967) *Proc. Nat. Acad. Sci. USA* 57, 233–235; (f) Schrader, E. (1963) *Annalen* 670, 133, reports mp of 102–104°C; (g) Iselin, B. & Schwyzer, R. (1961) *Helv. Chim. Acta* 44, 171; mention, but do not characterize, this compound.

(liquid film) 3340 cm⁻¹ (—NH); 1750, 1670 (C=O). The NMR (CCl₄, ppm): 0.92 (s, 9H); 1.65 (s, 9H); 3.74 (s, 3H); 3.80 (m, 2H); 4.95 (m, 1H); 5.9 (broad, 1H, NH). *Anal.* Calcd. for C₁₃H₂₃NO₅SSi: C, 46.87; H, 8.19; N, 4.56. Found: C, 46.71; H, 8.00; N, 4.47.

N-Thiol-*t*-BOC glycine from the free amino acid

A mixture of di-*t*-butyl dithiol dicarbonate (1.7 g) and glycine (0.5 g) in THF–H₂O (2:1, v/v) was refluxed for 18 hr. Treatment of the reaction mixture by method *B* gave 0.95 g (79%) of *N*-thiol-*t*-BOC glycine, mp 129–130°C (from CHCl₃). The properties were: IR (CHCl₃), 3400–2550 cm⁻¹ (broad, —NH and COOH); 1730, 1660 (C=O); NMR (CHCl₃); 1.51 (s, 9H); 4.06 (d, J = 5.5, 2H); 6.10 (broad, 1H, NH); 10.05 (s, 1H, COOH). *Anal.* Calcd. for C₇H₁₃NO₃S: C, 43.97; H, 6.85, Found: C, 44.10; H, 6.71.

Acidic removal of *N*-thiol-*t*-BOC group from *N*-thiol-*t*-BOC L-tyrosine methyl ester (7c)

This compound was unchanged by treatment with formic acid or by CF₃COOH–H₂O, under conditions that remove the *t*-BOC group.

N-thiol-*t*-BOC L-tyrosine methyl ester (7c) (0.2 g) was dissolved in a mixture of acetic acid (2 ml) and 30% H₂O₂ (1 ml). The solution was gently refluxed for 30 min and evaporated on a steam bath under reduced pressure. The resulting reddish-brown oil was cooled with ice and made basic with 3% NH₄OH. The solution was saturated with NaCl and extracted with CHCl₃; the CHCl₃ layer was dried and evaporated under reduced pressure. Solid (50 mg) was obtained. A sample recrystallized from EtOAc melted at 134–136°C and showed no depression of melting point in mixture with an authentic sample of L-tyrosine methyl ester; the IR spectrum and the optical rotation were identical with an authentic sample, indicating no racemization during formation or removal of the *N*-thiol-*t*-BOC group.

1. Dean, C. S., Tarbell, D. S. & Friederang, A. W. (1970) *J. Org. Chem.* 35, 3393–3397.
2. Dean, C. S. & Tarbell, D. S. (1971) *J. Org. Chem.* 36, 1180–1183.
3. Compound 3 has been reported in low yield by Howe, J. W. & Morris, L. R. (1962) *J. Org. Chem.* 27, 1901–1902.
4. Boehm, T. & Mehta, D. (1938) *Chem. Ber.* 71, 1797–1802.
5. Thoma, W. & Rinke, H. (1959) *Annalen* 624, 30–36.
6. Kollonitsch, J., Gabor, V. & Hajos, A. (1956) *Chem. Ber.* 89, 2288–2292, 2293–2301.
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8. For leading results and references, see Melchior, W. B., Jr. & Fahrney, D. (1970) *Biochemistry* 9, 251–258.
9. Leonard, N. J., McDonald, J. J., Henderson R. E. L. & Reichmann, M. E. (1971) *Biochemistry* 10, 3335–3342; Leonard, N. J., McDonald, J. J. & Reichmann, M. E. (1970) *Proc. Nat. Acad. Sci. USA* 67, 93–98.

Polymerization of Propylene with Tin Tetraalkyl-Titanium Tetrachloride Catalyst

By Nobuyuki Ashikari and Masakazu Honda

Many studies[1] on the catalyst for preparing polypropylene have been performed, since Natta obtained the polypropylene having high molecular weight and high stereoregularity. On the polymerization of propylene using tin tetraalkyl as a catalyst component, only a Du Pont patent[2] has been known. However, the description is so brief that the details are not explained. From our preliminary experiments of the polymerization of propylene using tin tetraalkyl in combination with titanium tetrachloride, titanium trichloride, dichlorodialkyl titanate, or tetraalkyl titanate, it was found that the effective catalyst was only the complex comprising titanium tetrachloride as a component. Moreover, when the catalyst was used as soon as the two components were mixed, the polymer produced thereby contained a greater part of low polymer. Accordingly, the polymerization in this study was performed considering the adequate times for the production of the complex.

Experimental and Results

Reaction between Tin Tetraalkyl and Titanium Tetrachloride.—The reaction between tin tetraalkyl and titanium tetrachloride does not proceed very fast, and so prolonged reaction times are required for the completion of the complex. The reaction rate depends, of course, upon the reaction temperature, the length of alkyl chain in the tin tetraalkyl, and the ratio of the catalyst components. Besides, the presence of a solvent will affect the reaction rate. However, the catalyst preparation in this study was performed without solvent, because the presence of the solvent makes the end-point of reaction obscure.

When the catalyst is prepared in a solvent without vigorous stirring, the product precipitates at the bottom of the vessel as an adhesive mass which can not be easily dispersed into the solvent. Generally, if the ratio of the two components deviates greatly from unity, both components still remain in liquid form after the reaction is over. Therefore, in this case, the end-point of reaction is not clear. On the other hand, when the ratio is about 1.0, the whole becomes solid exhibiting a comparatively apparent end-point. Therefore, the
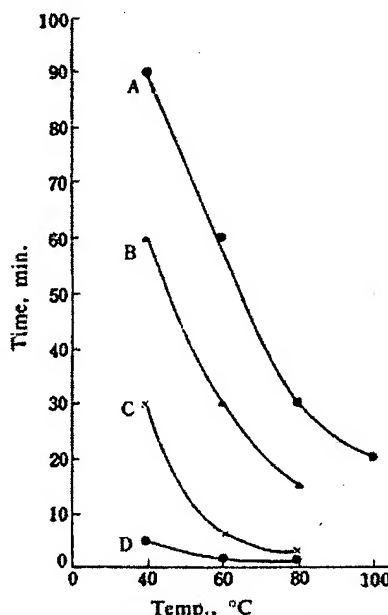
1) For example, G. Natta, I. Pasquon and E. Giachetti, *Angew. Chem.*, **69**, 213 (1957).

2) E. I. Du Pont de Nemours & Co., Brit. Pat. 777538 (June 26, 1957).

Fig. 1. Time required for the complex production.

A: *n*-Butyl	C: Isopropyl
B: *n*-Propyl	D: Ethyl

experiments for observing the times required for the production of the complex were carried out without any solvent at about equimolar composition of tin tetraalkyl and titanium tetrachloride. In Fig. 1, the effects of the alkyl radical in the tin tetraalkyl molecule and the reaction temperature upon the rate of the production of the complex are represented.

The vertical axis in Fig. 1 represents the times required for the solidifying of the two components which were mixed at a given temperature. The preparation of catalyst complex in the following experiments was performed referring to this condition; also analogously in the case where the ratio of the two component deviates passably from unity.

Polymerization Procedure.—In a cooled polymerization tube containing the complex which had been prepared by mixing the two components, a definite amount of monomer was introduced. The complex was shattered in a high speed shaker. In the case of polymerization in solution, the shattering of the complex was taken before the monomer

was introduced. The tube was immersed in a constant temperature bath. After the reaction proceeded for definite reaction times, the tube was cooled by dry ice-methanol, and vented. Then, the contents of the tube were treated with methanol acidified by hydrochloric acid to decompose the catalyst, washed with methanol several times, and dried under reduced pressure.

Measurement of Viscosity.—The viscosity of the polymer solution was measured using tetralin, as a solvent, which had been purified by distillation after being dried over sodium, using an improved Ubbelohde viscometer of dilution type, at $135 \pm 0.05°C$. The viscometer was filled with nitrogen during the measurement.

The molecular weight of the polymer was calculated using Ciampa's equation[3] shown below.

$$[\eta] = 0.25 \times 10^{-4} M$$

Dependence of Conversion and Insoluble Part of Polymer in Boiling n-Hexane on the Composition of Catalyst. — The influence of the ratio of catalyst components upon the conversion and the insoluble part of polymer in boiling n-hexane was investigated by the polymerization using a catalyst complex of tin tetraethyl-titanium tetrachloride. In each experiment, 5 g. of monomer was polymerized with a catalyst containing 9.26×10^{-2} mol. of titanium tetrachloride and a definite amount of tin tetraethyl (which is represented in Table I), in 5 cc. of n-hexane at 30°C for 25 hr. The Results are shown in Table I.

TABLE I. EFFECT OF THE RATIO OF COMPONENTS IN THE COMPLEX UPON THE CONVERSION AND THE INSOLUBLE PART IN BOILING n-HEXANE

No.	SnR₄/TiCl₄	Conversion %	Insoluble part in n-hexane, %
1	0.54	4.01	8.61
2	0.82	2.72	11.52
3	1.09	0.71	12.21
4	1.36	2.11	15.14
5	1.64	15.75	18.32
6	1.91	8.73	17.26

TiCl₄; 9.26×10^{-2} mol.. Monomer; 5 g.
n-Hexane; 5 cc., Temp.; 30°C.

It is seen that a minimum for the rate of polymerization exists where the ratio of tin tetraethyl to titanium tetrachloride is about unity. This respect is discussed afterward.

Effects of Alkyl Radical in SnR₄ and the Temperature of Complex Preparation upon the Conversion and the Molecular Weight of Polymer.—In each experiment, 15 g. of monomer was polymerized with the catalyst which was prepared by mixing the two components, i.e., 2.024×10^{-2} mol. of tin tetraalkyl and 1.852×10^{-2} mol. of titanium tetrachloride, in a sealed tube at 40°C for 15 hr. Each polymer was then extracted by boiling n-hexane. This procedure was made to find the percentage of so-called isotactic polymer which had been defined by

Natta as an isoluble part in boiling n-heptane. In this sence, the extraction has to be made, if possible, by n-heptane. However, the greater part of the polymer which would be extracted by boiling n-heptane is also extracted by boiling n-hexane, as is shown in Table III. Accordingly, the solvent, n-hexane was used. These results are shown in Table II.

The effect of the temperature of catalyst preparation upon the conversion is represented in Fig. 2.
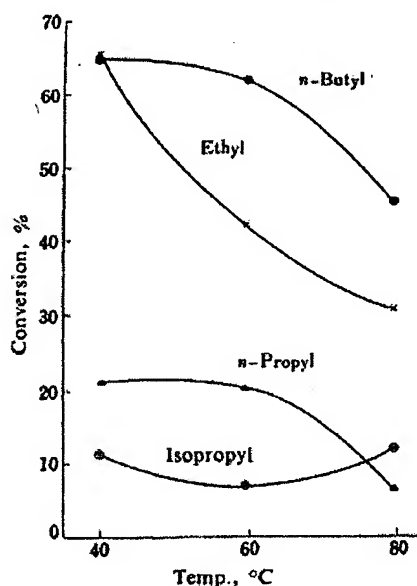

Fig. 2. Effect of the temperature of the catalyst preparation upon the conversion.

The polymerization with the catalyst prepared at lower temperature resulted in higher conversion, which gave lower molecular weight and further lower percentage of polymer insoluble in boiling n-hexane (except for the case of tin tetraethyl).

Extraction of the Polymer with Various Solvents. — To find the percentage of atactic and isotactic parts which are contained in the polymer prepared with the tin tetraethyl-titanium tetrachloride catalyst, 55.774 g. of the polymer was successively extracted by such series of solvents as acetone, diethyl ether, n-hexane, and n-heptane. The sample employed in this extraction was prepared by polymerizing 75 g. of monomer with the catalyst which had been prepared at 20°C by the reaction between 1.012 mol. of tin tetraethyl and 0.926 mol. of titanium tetrachloride. In this polymerization reaction (at 40°C, for about 15 hr.), 57.428 g. of the polymer was obtained (conversion; 76.6%). The viscosity of each fraction was measured by means of the aforementioned method. These results are shown in Table III.

It[4] has already been known that an organo

3) G. Ciampa, Chim. e ind. (Milan), 38. 298 (1956).

4) N. G. Gaylord and H. F. Mark, "Linear and Stereoregular Addition Polymers" Interscience Publishers, Inc., New York (1959), p. 129.

APPENDIX II

TABLE II. POLYMERIZATIONS AT VARIOUS TEMPERATURES USING VARIOUS TIN TETRAALKYLS

R in SnR$_4$	Cat. preparation temp., °C	Conversion %	Insoluble part (%) in boiling hexane	$[\eta] \times 10$	$M \times 10^{-3}$
Ethyl	40	65.7	18	2.4	9.7
″	60	42.5	12	1.5	6.2
″	80	31.6	14	1.9	5.1
n-Butyl	40	65.4	4	0.8	3.2
″	60	62.4	3	1.0	4.1
″	80	45.7	5	1.4	5.6
Isopropyl	40	11.5	—	0.4	1.4
″	60	7.4	—	0.4	1.7
″	80	12.1	—	0.3	1.1
n-Propyl	40	21.1	2.6	0.8	3.2
″	60	20.4	4.2	1.1	4.0
″	80	6.4	4.0	1.3	5.1

The viscosity was measured for the original polymer.
Monomer : 15 g., Temp. ; 40°C, Time ; 15 hr.
SnR$_4$; 2.024×10^{-2} mol., TiCl$_4$; 1.852×10^{-2} mol.
The polymers prepared with Sn(i-C$_3$H$_7$)$_4$-TiCl$_4$ were grease-like, and so, the extractions were not carried out.

TABLE III. EXTRACTION WITH VARIOUS SOLVENTS

Solvent	Polymer, g.	Fraction, %	$[\eta]$	$M \times 10^{-3}$	M. p., °C
Acetone	2.584	4.6	—	—	
Ether	22.370	40.1	0.11	4.4	
n-Hexane	20.363	40.4	0.13	5.2	
n-Heptane	2.036	3.7	0.26	10.4	120
(Residue)	6.255	11.2	1.02	40.8	155~160

metallic compound containing the metal with smaller ionic radius, results in a higher yield of isotactic polymer. Accordingly, it is natural that the polymerization using a compound of tin as a catalyst component results in a lower yield of isotactic polymer.

Rate of Polymerization.—In order to find the rate of polymerization, the following experiment was performed. Each polymerization was carried out in a sealed tube with tin tetraethyl-titanium tetrachloride catalyst consisting of 2.024×10^{-2} mol. of the former and 1.852×10^{-2} mol. of the latter. The catalyst was shattered finely by a high speed shaker in 15 cc. of n-hexane before the monomer (10 g.) was introduced. The polymers were treated by means of the aforementioned method. The relation between the conversion and the reaction time is represented in Fig. 3.
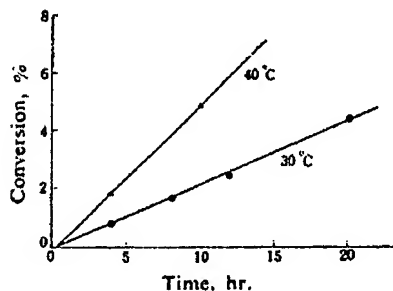
The rates at 30 and 40°C were calculated from Fig. 3 as 0.22%-conversion/hr. and 0.5%-conversion/hr., respectively. The values indicate that the polymerization of propylene with tin tetraalkyl-titanium tetrachloride catalyst proceeds very slowly in the solution system.

Infrared Spectra. — In order to compare the microstructure of the polymer prepared by the tin tetraethyl-titanium tetrachloride catalyst with that
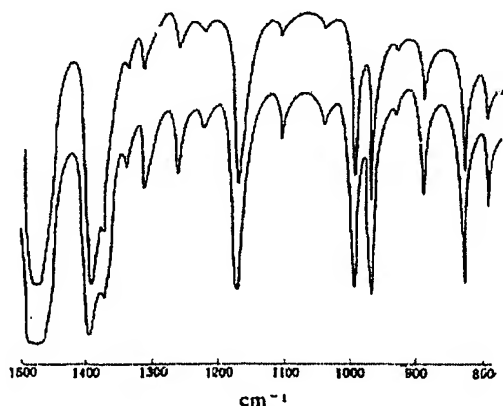

Fig. 3. Polymerization rate in n-hexane.

Fig. 4. Infrared spectra of in boiling heptane insoluble polymers.

A: Polymer prepared with SnR$_4$-TiCl$_4$
B: Moplen

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of ' Moplen ', the polymer prepared by aluminium-trialkyl-titanium trichloride catalyst, the infrared spectrum of the insoluble part in boiling n-heptane was observed. B is a spectrum of n-heptane insoluble part of Moplen. From the comparison of A with B, it is obvious that these polymers are strikingly similar in their microstructures.

Discussion

Generally, the Ziegler catalyst consists of Lewis acid and Lewis base. Therefore, a cationic or an anionic reaction will predominantly occur according to the catalyst composition in which Lewis acid or base is contained in excess, respectively.

The double bond of propylene, of course, is easily attacked by a cationic catalyst, owing to the effect of the methyl group. Moreover, it is also well known that, in the case of cationic polymerization, the growth of the chain easily terminates by a chain transfer. Thus, the rate of cationic polymerization is steady, but the polymer produced has usually a low molecular weight and further low stereoregularity. On the other hand, in the case of anionic polymerization, a polymer having a high molecular weight and further high stereoregularity is usually obtained, while the rate of reaction becomes smaller than that of cationic reaction.

From the facts mentioned above, it may be said that the decrease of conversion (from No. 1 to No. 3) with an increase in the amount of tin tetraethyl will mean that the cationic character is replaced gradually by the anionic character. It is also considered that, in Nos. 3—6, the effective anionic catalyst increases with the increase of the amount of tin tetraethyl.

Next we discuss the effects of temperature of catalyst preparation upon the convertion, the insoluble part in boiling n-hexane and stereospecificity. As is apparent from Fig. 1, the reducing power is the strongest in the case of tin tetraethyl, so that the effective anionic catalyst will be produced even at a lower temperature, in such a case. The fact that both the conversion and the stereospecificity decrease with an increase in the temperature will mean a decreasing of the active center which is in suitable valence state.

In the case of the propyl or butyl radical, the reducing power is so much weaker than that of the ethyl radical, that a temperature which is suitable for preparing the effective complex containing the latter, is unsuitable for producing the effective one containing the former. At such a lower temperature, the somewhat cationic character will still remain in the complex. When the temperature becomes higher, the cationic character will decrease, and so the conversion decreases while the stereospecificity increases, as is seen in Table II.

In regard to the effects of the length of the alkyl radical upon the conversion and the stereospecificity, no distinct relations between them were obtained.

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APPENDIX III

United States Patent [19]

Kohara et al.

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[45] Date of Patent: **Jul. 23, 1991**

[54] **PROCESS FOR PRODUCING POLYMER BY RING-OPENING POLYMERIZATION**

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[21] Appl. No.: 553,849

[22] Filed: Jul. 18, 1990

[30] **Foreign Application Priority Data**

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[51] Int. Cl.^{5} C08F 4/44; C08F 136/00
[52] U.S. Cl. 526/114; 526/283
[58] Field of Search 526/90, 114; 525/297

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[57] **ABSTRACT**

A process for producing a polymer by ring-opening polymerization of a norbornene-type monomer, which comprises starting the ring-opening polymerization in the presence of a Ziegler-type catalyst consisting essentially of an organometallic compound of a metal belonging to the groups I to III of the periodic table and titanium tetrahalide, carrying out the ring-opening polymerization until the norbornene-type monomer shows a conversion ratio of not less than 60%, and then adding a tungsten and/or molybdenum-based metathesis catalyst to the polymerization reaction system to continue the ring-opening polymerization.

20 Claims, No Drawings

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PROCESS FOR PRODUCING POLYMER BY RING-OPENING POLYMERIZATION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for producing a polymer by ring-opening polymerization of a norbornene-type monomer, more specifically to a process for producing a polymer having a limited distribution of molecular weight by ring-opening polymerization at high yields.

2. Related Art

In recent years, attention has been paid to hydrogenated products of polymers produced by ring-opening polymerization of norbornene-type monomers such as tetracyclododecene, dicyclopentadiene (DCP), tricyclopentadiene, etc., as an optical material for use in an optical disk, optical lens, transparent film, etc. (e.g. JP-A-60-26024, JP-A-1-24826, WO80/01953, EP303,246, EP317,262). The reasons therefor are that such hydrogenated products are excellent in transparency and heat resistance and hardly susceptible to water and that they have comparatively small birefringence and excellent moldability.

The ring-opening polymerization of a norbornene-type monomer is carried out, in general, in the presence of (1) a catalyst system consisting of an organometallic compound such as an organoaluminum compound and a tungsten and/or molybdenum-based metathesis catalyst (e.g. U.S. Pat. No. 3,557,072) or (2) a catalyst system containing an organometallic compound such as an organoaluminum compound and a transition-metal compound such as titanium tetrahalide (e.g. JP-B-41-20111, DE-A-2,502,748).

However, in the case of the ring-opening polymerization using the above (1) catalyst system, the resultant polymer has a broad distribution of molecular weight and therefore has large birefringence, in spite of an advantage that the polymer can be obtained at such high yields that the residual monomer is hardly present in the reaction system when the reaction has completed.

In the case of the ring-opening polymerization using the above (2) catalyst system, the molecular weight distribution of a resulting polymer can be easily controlled. However, with a decreasing concentration of a monomer in the reaction system, the polymer formation ratio decreases markedly. Even if the polymerization is started with a high monomer concentration, the polymer formation ratio decreases as the monomer concentration decreases with the progress of the polymerization reaction. Hence, the polymer formed by the ring-opening polymerization of the present catalyst system cannot be obtained at high yields. Moreover, a large amount of an unreacted monomer remains in the reaction system when the polymerization has completed. It is very difficult to remove this remaining monomer at a polymer-isolation step. And, the unreacted monomer remaining in the polymer causes voids, a phenomenon of haze on a molded article surface called flash or silver lines called silver streaks.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a process for ring-opening polymerization of a norbornene-type monomer, in which a polymer having a limited distribution of molecular weight can be obtained, the concentration of the monomer remaining in the reaction sys-

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tem when the polymerization has completes is very low, and the polymer can be produced at high yields.

The present inventors made an intensive study in order to overcome the above prior art problems, and found that the above object can be achieved by a combination process of a first step (anterior polymerization step) of starting ring-opening polymerization of a norbornene-type monomer in the presence of a Ziegler-type catalyst consisting essentially of an organometallic compound of a metal belonging to the groups I to III of the periodic table and titanium tetrahalide and a second step (posterior polymerization step) of continuing the ring-opening polymerization by adding a tungsten and-/or molybdenum-based metathesis catalyst to the reaction system during the reaction.

According to this invention, therefore, there is provided a process for producing a polymer by ring-opening polymerization of a norbornene-type monomer, which comprises starting the ring-opening polymerization in the presence of a Ziegler-type catalyst consisting essentially of an organometallic compound of a metal belonging to the groups I to III of the periodic table and titanium tetrahalide, carrying out the ring-opening polymerization until the norbornene-type monomer shows a conversion ratio of not less than 60%, and then adding a tungsten and/or molybdenum metathesis catalyst to the reaction system to continue the ring-opening polymerization.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

This invention will be detailed hereinbelow.

Norbornene-type monomer

Examples of the norbornene-type monomer are norbornene and alkyl, alkylidene and/or aryl-substituted compounds thereof such as 5-methyl-2-norbornene, 5,6-dimethyl-2-norbornene, 5-ethyl-2-norbornene, 5-butyl-2norbornene, 5-ethylidene-2-norbornene, 5-phenyl-2-norbornene; dicyclopentadiene, 2,3-dihydrodicyclopentadiene and substituted compounds of these with alkyl such as methyl, ethyl, propyl, butyl or the like; dimethanooctahydronaphthalene and alkyl, alkylidene and/or aryl-substituted compound thereof such as 6-methyl-1,4:5,8-dimethano-1,4,4a,5,6,7,8,8a-octahydronaphthalene, 6-ethyl-1,4:5,8-dimethano-1,4,4a,5,6,7,8,8a-octahydronaphthalene, 6-ethylidene-1,4:5,8-dimethano-1,4,4a,5,6,7,8,8a-octahydronaphthalene; 6-phenyl1,4:5,8-dimethano-1,4,4a,5,6,7,8,8a-octahydronaphthalene, etc.; trimers and tetramers of cyclopentadiene such as 4,9:5,8-dimethano-3a,4,4a,5,8-,8a,9,9a-octahydro-1H-benzoindene, 4,11:5,10:6,9-trimethano-3a,4,4a,5,5a,6,-9,9a,10,10a, 11,11a-dodecahydro-1H-cyclopentaanthrace, etc.

The norbornene-type monomer may have a polar substituent or a substituent having a metal atom. Examples of such a substituent are halogen atoms such as chlorine, bromine and fluorine; ester-type moieties such as methoxycarbonyl, ethoxycarbonyl and acetoxy groups; a cyano group; a pyridyl group; silyl groups such as trimethylsilyl, triethylsilyl and dimethylmonochlorosilyl groups; and the like.

These norbornene-type monomers may be used alone or in combination. In order to impart excellent heat resistance to the polymer formed by ring-opening polymerization and the hydrogenation product thereof by adjusting the glass transition point (Tg) thereof to not

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less than 100° C., tetracyclic or pentacyclic compounds of these norbornene-type monomers are used alone or as a main component in combination with bicyclic or tricyclic monomers. In view of birefringence in particular, a homopolymer or copolymer of lower alkyl-substituted or alkenyl-substituted tetracyclic compounds is preferable. Above all, a homopolymer of a substituted compound having a substituent having 1 to 3 carbon atoms or a copolymer containing as a copolymerizing component, not less than 50% by weight, preferably not less than 70% by weight, of said substituted compound is preferred.

And, as a copolymerizing component, it is possible to use other cycloolefins such a cyclopropene, cyclobutene, cyclopentene, cycloheptene, cyclooctene, 5,6-dihydrodicyclopentadiene, etc., in such an amount that does not impede the object of this invention, usually in the range of not more than 30% by weight.

Further, as a molecular-weight regulator, noncyclic olefins may be used in a small amount, usually in the range of up to 10 mol %. In particular, α-olefins such as 1-butene, 1-pentene, 1-hexene, etc., are preferred.

Ring-opening polymerization catalyst

Ziegler-type catalyst

(a) Organometallic compounds

Examples of the organometallic compound of a metal belonging to the groups I to III of the periodic table, used in this invention, are organoaluminum compounds, organolithium compounds, organomagnesium compounds, etc., as are described in JP-B-41-20111, DE-A-2502748 and U.S. Pat. No. 3,557,072. Of these compounds, organoaluminum compounds are preferred.

Examples of the organoaluminum compounds are trimethylaluminum, triethylaluminum, tri-n-propylaluminum, triisopropylaluminum, triisobutylaluminum, trihexylaluminum, trioctylaluminum, triphenylaluminum, tribenzylaluminum, diethylaluminum monochloride, di-n-propylaluminum monochloride, diisobutylaluminum monochloride, di-n-butylaluminum monochloride, diethylaluminum monobromide, diethylaluminum monoiodide, diethylaluminum monohydride, di-n-propylaluminum monohydride, diisobutylaluminum monohydride, methylaluminum sesquichloride, ethylaluminum sesquibromide, isobutylaluminum sesquichloride, ethylaluminum dichloride, ethylaluminum dibromide, propylaluminum dichloride, isobutylaluminum dichloride, ethylaluminum dibromide, ethylaluminum diiodide, lithiumaluminum tetra-n-butyl, etc.

Examples of the organolithium compounds are methyllithium, ethyllithium, n-butyllithium, n-hexyllithium, etc.

Examples of the organomagnesium compounds are diethylmagnesium, methylmagnesium iodide, ethylmagnesium bromide, methylmagnesium bromide, n-propylmagnesium chloride, t-butylmagnesium chloride, allylmagnesium chloride, phenylmagnesium bromide, etc.

(b) Titanium tetrahalide

Specific examples of the titanium tetrahalide are titanium tetrachloride, titanium tetrabromide, etc.

(c) Amine-type activator

The Ziegler-type catalyst of this invention may be used in combination with an amine-type activator.

Examples of the amine-type activator are aliphatic, alicyclic or aromatic tertiary amines and heterocyclic

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amines. Specific examples thereof are trimethylamine, triethylamine, tripropylamine, tri-n-butylamine, dimethylaniline, pyridine, α-picoline, γ-picoline, 2,6-lutidine, etc., (DE-A-2,502,748, WO89/01953).

Metathesis catalyst

Examples of the tungsten and/or molybdenum-based metathesis catalyst are halides, oxyhalides or oxyorganic compounds of these metals. Specific examples thereof are tungsten hexachloride, tungsten (IV) oxychloride, tungsten tetrachloride, molybdenum pentachloride, acetylacetonatomolybdenum oxide, etc.

Conditions for ring-opening polymerization

Solvent

The ring-opening polymerization of the norbornene-type monomer in this invention may be carried out in the absence of a solvent. In general, however, it is carried out in an inert organic solvent.

As the solvent, hydrocarbon solvents are preferred, and of these solvents, cyclic hydrocarbon solvents having the excellent power to dissolve the polymers being formed by the ring-opening polymerization are particularly preferred.

Specific examples thereof are aromatic hydrocarbons such as benzene, ethylbenzene, toluene, xylene, etc.; aliphatic hydrocarbons such as n-pentane, hexane, heptane, etc.; alicyclic hydrocarbons such as cyclopentane, cyclohexane, methylcyclohexane, dimethylcyclohexane, decalin, etc.; hydrocarbon halides such as methylene dichloride, dichloroethane, dichloroethylene, tetrachloroethane, chlorobenzene, dichlorobenzene, trichlorobenzene, etc. These may be used in combination.

The amount of the solvent, based on 1 part by weight of the monomer, is usually 1 to 20 parts by weight, preferably 2 to 10 parts by weight.

Polymerization temperature

The temperature conditions for the ring-opening polymerization are not specially limited, and any temperature between −20° C. and 100° C., usually between 0° C. and 100° C., preferably between 10° C. and 80° C. is selected.

Pressure for polymerization system

The pressure for the polymerization is 0 to 50 kg/cm², usually ordinary pressure to 10 kg/cm², preferably not more than 5 kg/cm².

Atmosphere for polymerization system

The ring-opening polymerization is usually carried out in atmosphere of an inert gas such as nitrogen, argon, or the like.

Addition of ring-opening polymerization catalysts

The amounts of the ring-opening polymerization catalysts are as follows. Concerning the amount of each of the components of the Ziegler-type catalyst per 100 moles of the monomer, the amount of the (a) organometallic compound is 0.1 to 10 moles, preferably 0.5 to 5 moles, the amount of the (b) titanium tetrahalide per 100 moles of the monomer is 0.05 to 5 moles, preferably 0.25 to 2.5 moles, and the amount of the (c) amine-type activator per 100 moles of the monomer, if used, is 0.2 to 20 moles, preferably 1 to 10 moles. And, the amount of the

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metathesis catalyst per 100 moles of the monomer is 0.005 to 1 mole, preferably 0.01 to 0.5 mole.

Further, the proportions of each of the above components (a), (b) and (c) and the metathesis catalyst are as follows. Per mole of the (a) organometallic compound, the proportion of the (b) titanium tetrahalide is 0.05 to 1 mole, preferably 0.1 to 0.9 mole, that of the (c) amine-type activator 0.5 to 10 moles, preferably 1 to 5 moles, and that of the metathesis catalyst is 0.002 to 0.5 mole, preferably 0.01 to 0.1 mole.

In this invention, at first, the ring-opening polymerization of the norbornene-type monomer is started in the presence of the Ziegler-type catalyst, and in course of the reaction, the tungsten and/or molybdenumbased metathesis catalyst is added to the reaction system to continue the ring-opening polymerization.

If these catalysts are added in some other order than above, the object of this invention cannot be achieved.

When only the Ziegler-type catalyst is used, or when the metathesis catalyst is not added in the posterior polymerization step, the conversion ratio of the monomer is as low as about 90% at best, and the polymer cannot be obtained at high yields. When the ring-opening polymerization is carried out in the presence of the metathesis catalyst only, the resultant polymer has a broad distribution of molecular weight. And, even if the Ziegler-type catalyst is added after the ring-opening polymerization has been started by using the metathesis catalyst, it is impossible to control the molecular weight distribution to a preferred range. Further, even if the ring-opening polymerization is started in the presence of both the Ziegler-type catalyst and the metathesis catalyst, the result is none the better.

The metathesis catalyst in the posterior polymerization step is added at a time when the conversion ratio of the norbornene-type monomer becomes not less than 60%, preferably not less than 70% after the ring-opening polymerization is started in the presence of the Ziegler-type catalyst, preferably in the presence of $R_3Al/$-$TiCl_4$/amine activator. If the metathesis catalyst is added when the conversion ratio is too low, it is difficult to control the molecular weight and molecular weight distribution of the resulting polymer. The upper limit of the conversion ratio in the anterior polymerization step is about 90%.

After the addition of the metathesis catalyst, the ring-opening polymerization in the posterior polymerization step is continued until the final conversion ratio becomes, preferably, not less than 95%.

Polymer formed by ring-opening polymerization

The polymer produced by ring-opening polymerization according to this invention has a number average molecular weight (Mn) of 10,000 to 200,000, preferably 20,000 to 100,000, a molecular distribution (Mw/Mn) of not more than 3, preferably 2.5. When the polymer is hydrogenated and used as an optical material such as an optical disk, the polymer having a number average molecular weight (Mn) of 20,000 to 40,000 is the most preferred.

When the number average molecular weight is larger than the above range, the polymer has large birefringence and poor moldability. When it is smaller than the above range, the polymer has poor mechanical strength. And, when the molecular weight distribution (Mw/Mn) is greater than the above range, the polymer has large birefringence.

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The above-specified molecular weight and molecular weight distribution of the polymer are according to gel-permeation chromatography ("GPC" hereinbelow) analysis using cyclohexane as a solvent.

The polymer formed by the ring-opening polymerization is hydrogenated according to an ordinary method and can be suitably used as an optical material for an optical disk, optical lens, transparent film, and the like.

EXAMPLES

This invention will be explained more specifically by reference to Examples. However, this invention shall not be limited only thereto.

EXAMPLE 1

52.2 g (300 mmol) of 6-methyl-1,4:5,8-dimethano-1,4,4a,5,6,7,8,8a-octahydronaphthalene ("MTD" hereinbelow) was dissolved in 150 ml of cyclohexane. And, as a polymerization solvent, 6.84 g (9.0 mmol) of a solution of 15% by weight of triethylaluminum in cyclohexane, 2.7 g (27 mmol) of triethylamine and 5.7 g (6.0 mmol) of a solution of 20% by weight of titanium tetrachloride in cyclohexane were added in the presence of 0.25 g (3.0 mmol) of 1-hexene as a molecular weight regulator at 30° C. to start ring-opening polymerization.

When 30 minutes passed after the polymerization was started, the conversion ratio reached 86%. At this time, 6.6 g (0.15 mmol) of a solution of 0.9% by weight of tungsten hexachloride in cyclohexane was added to continue the polymerization further for 30 minutes.

The reaction was stopped by adding 4 ml of methanol, and the reaction solution was poured into 5 l of isopropyl alcohol to coagulate the resultant polymer. The coagulated polymer was dried under vacuum to give 50.6 g of a polymer formed by the ring-opening polymerization. The yield of the polymer was 97%.

During the polymerization, when 30 minutes passed after the titanium tetrachloride was added and when 30 minutes passed after the tungsten hexachloride was added, 2 ml each of samples of the polymerization solution were taken and subjected to GPC analysis to measure molecular weights, molecular weight distributions and conversion ratios of the monomer to the polymer.

GPC analysis conditions: Measurements were made with HLC802L (supplied by TOSOH CORPORATION) having TSK gel G5000H-G4000H column at a temperature of 38° C. and a flow rate of 1.0 ml/minute by using toluene or cyclohexane as a solvent. Toluene was used as a solvent for the measurement of the molecular weights and molecular weight distributions, and cyclohexane for the conversion ratios.

Table 1 shows the results.

Examples 2–4

Example 1 was repeated except that the proportions of the Ziegler-type catalyst and metathesis catalyst were changed as shown in Table 1. Table 1 shows the results.

Example 5

Example 1 was repeated except that the tungsten hexachloride was replaced with 0.30 mmol of molybdenum pentachloride. Table 1 shows the results.

Example 6

Example 1 was repeated except that the monomer was changed to a mixture of MTD (240 mmol) with norbornene ("NB" hereinbelow) (60 mmol) and that the

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(12) **United States Patent**
Margrave et al.

(10) Patent No.: **US 6,827,918 B2**
(45) Date of Patent: *Dec. 7, 2004

(54) **DISPERSIONS AND SOLUTIONS OF FLUORINATED SINGLE-WALL CARBON NANOTUBES**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 561 days.

This patent is subject to a terminal disclaimer.

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(22) Filed: **Mar. 16, 2001**

(65) **Prior Publication Data**

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(62) Division of application No. 09/787,473, filed as application No. PCT/US99/21366 on Sep. 17, 1999

(60) Provisional application No. 60/101,092, filed on Sep. 18, 1998, provisional application No. 60/106,918, filed on Nov. 3, 1998, and provisional application No. 60/138,505, filed on Jun. 10, 1999.

(51) Int. Cl.^{7} D01F 9/12
(52) U.S. Cl. 423/447.1
(58) Field of Search 423/447.1, 460

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(57) **ABSTRACT**

This invention is directed to making chemical derivatives of carbon nanotubes and to uses for the derivatized nanotubes, including making arrays as a basis for synthesis of carbon fibers. In one embodiment, this invention also provides a method for preparing single wall carbon nanotubes having substituents attached to the side wall of the nanotube by reacting single wall carbon nanotubes with fluorine gas and recovering fluorine derivatized carbon nanotubes, then reacting fluorine derivatized carbon nanotubes with a nucleophile. Some of the fluorine substituents are replaced by nucleophilic substitution. If desired, the remaining fluorine can be completely or partially eliminated to produce single wall carbon nanotubes having substituents attached to the side wall of the nanotube. The substituents will, of course, be dependent on the nucleophile, and preferred nucleophiles include alkyl lithium species such as methyl lithium. Alternatively, fluorine may be fully or partially removed from fluorine derivatized carbon nanotubes by reacting the fluorine derivatized carbon nanotubes with various amounts of hydrazine, substituted hydrazine or alkyl amine. The present invention also provides seed materials for growth of single wall carbon nanotubes comprising a plurality of single wall carbon nanotubes or short tubular molecules having a catalyst precursor moiety covalently bound or physisorbed on the outer surface of the sidewall to provide the optimum metal cluster size under conditions that result in migration of the metal moiety to the tube end.

54 Claims, 26 Drawing Sheets

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monolayer extending in directions substantially perpendicular to the orientation of the individual nanotubes. In this process the seed array tubes are opened at the top (free) end and a catalyst cluster is deposited at this free end. A gaseous carbon source is then provided to grow the nanotube assembly into a fiber. In various processes involving metal cluster catalysis, it is important to provide the proper number of metal atoms to give the optimum size cluster for single wall nanotube formation.

Derivatization of Single-wall Nanotubes

Since the discovery of single wall carbon nanotubes (SWNTs) in 1993 (Iijima, S. and Ichihashi, T., *Nature* 1993,363:603–605), researchers have been searching for ways to manipulate them chemically. While there have been many reports and review articles on the production and physical properties of carbon nanotubes, reports on chemical manipulation of nanotubes have been slow to emerge. There have been reports of functionalizing nanotube ends with carboxylic groups (Rao, et al., *Chem. Commun.*, 1996, 1525–1526; Wong, et al., *Nature*, 1998,394:52–55), and then further manipulation to tether them to gold particles via thiol linkages (Liu, et al., *Science*, 1998, 280:1253–1256). Haddon and co-workers (Chen, et al., *Science*, 1998, 282:95–98) have reported solvating SWNTs by adding octadecylamine groups on the ends of the tubes and then adding dichlorocarbenes to the nanotube side wall, albeit in relatively low quantities (~2%). While theoretical results have suggested that functionalization of the nanotube side-wall is possible (Cahill, et al., *Tetrahedron*, 1996, 52 (14):5247–5256), experimental evidence confirming this theory has not been obtained.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a method for derivatizing carbon nanotubes, especially the side walls of single-wall carbon nanotubes.

It is another object of this invention to provide a high yield, single step method for producing large quantities of continuous macroscopic carbon fiber from single-wall carbon nanotubes using inexpensive carbon feedstocks at moderate temperatures.

It is yet another object of this invention to provide macroscopic carbon fiber made by such a method. These and other objects of this invention are met by one or more of the following embodiments.

This invention provides single wall carbon nanotubes and/or tubular carbon molecules derivatized with substituents covalently bonded to carbon atoms of the side wall of the nanotube or molecule. The substituents may in principle be attached on the interior and/or exterior of the nanotube side wall, but the attachment will not be predominantly on the exterior wall. In particular, the single wall carbon nanotubes may have substituents selected from fluorine, alkyl and phenyl attached to the side wall. Such single wall carbon nanotubes having fluorine covalently bonded to the side wall of the nanotube demonstrate high electrical resistance.

This invention also provides a method for derivatizing carbon nanotubes comprising reacting carbon nanotubes with fluorine gas, the fluorine gas preferably being free of F_2. Where the carbon nanotubes are single wall nanotubes, and the temperature is at least 500° C., the product may be multiple wall carbon nanotubes derivatized with fluorine. Where the carbon nanotubes are single wall nanotubes, and the temperature is between 250° C. and 500° C., the product is single wall carbon nanotubes having fluorine covalently bonded to carbon atoms of the side wall of the nanotube.

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In one embodiment, this invention also provides a method for preparing single wall carbon nanotubes having substituents attached to the side wall of the nanotube by reacting single wall carbon nanotubes with fluorine gas and recovering fluorine derivatized carbon nanotubes, then reacting fluorine derivatized carbon nanotubes with a nucleophile. Some of the fluorine substituents are replaced by nucleophilic substitution. If desired, the remaining fluorine can be completely or partially eliminated to produce single wall carbon nanotubes having substituents attached to the side wall of the nanotube. The substituents will, of course, be dependent on the nucleophile, and preferred nucleophiles include alkyl lithium species such as methyl lithium. Alternatively, fluorine may be fully or partially removed from fluorine derivatized carbon nanotubes by reacting the fluorine derivatized carbon nanotubes with various amounts of hydrazine, substituted hydrazine or alkyl amine.

This invention also provides a process for preparing a suspension or solution of single wall carbon nanotubes in various solvents from which individual single wall carbon nanotubes may be isolated, the process comprising providing a mass of single wall carbon nanotubes that include bundles of fibers held in close association by van der Waals forces, derivatizing the side walls of the single wall carbon nanotubes with a plurality of chemical moieties distributed substantially uniformly along the length of said single wall carbon nanotube side walls, said chemical moieties having chemical and steric properties sufficient to prevent the reassembly of van der Waals force bound bundles, producing true solutions and recovering the individual, derivatized single wall carbon nanotubes from said solution or suspension. Preferably, the attached chemical moieties are fluorine to provide solution in various alcohols, preferably isopropyl alcohol, and various R-groups to appropriate to provide solubility in other solvents including $CHCl_3$, Dimethylformamide, etc.

In another embodiment, a method for forming a macroscopic molecular array of tubular carbon molecules is disclosed. This method includes the steps of providing at least about 10^6 tubular carbon molecules of substantially similar length in the range of 50 to 500 nm; introducing a linking moiety onto at least one end of the tubular carbon molecules; providing a substrate coated with a material to which the linking moiety will attach; and contacting the tubular carbon molecules containing a linking moiety with the substrate.

The present invention also provides seed materials for growth of single wall carbon nanotubes comprising a plurality of single wall carbon nanotubes or short tubular molecules having a catalyst precursor moiety covalently bound or physisorbed on the outer surface of the sidewall to provide the optimum metal cluster size under conditions that result in migration of the metal moiety to the tube end.

This invention also provides a seed array for the catalytic production of assemblies of single wall carbon nanotubes comprising a plurality of relatively short single wall carbon nanotubes assembled in a generally parallel configuration, and disposed on the side wall of each said single wall carbon nanotube a sufficient quantity of physisorbed or covalently bonded transition metal catalyst precursor moieties to provide active catalyst metal atom clusters of the proper size to grow single wall carbon nanotubes under conditions that promote the generation of metal atoms and the migration of said metal atoms to the free ends of said single wall carbon nanotubes.

In another embodiment, a method for continuously growing a macroscopic carbon fiber comprising at least about 10^6

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Gravimetric and electron microprobe analysis demonstrated that large amounts of fluorine can be added to SWNT. Resistance measurements along with vibrational spectroscopy (Raman, IR) confirm the formation of new chemical bonds to the nanotube superstructure. Contributions of absorbed molecular fluorine to the overall fluorine uptake are precluded at these temperatures (Watanabe, et al., 1988). It may be concluded, therefore, that fluorine is being covalently attached to the side wall of the SWNT.

TEM studies have shown that at fluorination temperatures as high as 325° C., the majority of the fluorination product maintains a tube-like structure. These studies also indicate that at 500° C., the single wall tubular structure does not survive the fluorination process and that some MWNT-like structures are being formed.

From the product stoichiometries, resistance measurements and IR spectra it is clear that reaction temperatures in excess of 150° C. allow one to covalently add significant amounts of fluorine to the tube wall. The small amount of fluorine that does show up in the product of the 150° C. fluorination reaction could be attributed to a combination of absorbed fluorine and fluorination of the end caps of the SWNT.

Fluoride can also be effectively removed from the SWNT using anhydrous hydrazine and that the rejuvenated product is in fact a SWNT. The inventors have found that, once fluorinated, SWNT can be defluorinated with anhydrous hydrazine via the following reaction: $CF_n+(n/4)N_2H_4 \rightarrow C+nHF+(n/4)N_2$. From the results of these defluorination experiments and the Raman and SEM studies associated with them, it appears that a majority of the tubes are destroyed at fluorination temperatures of above 400° C., whereas only a slight amount of tube destruction occurs at 250° C.

For reactions in which only the outside of the tube is being fluorinated (the SWNT used in this study were closed at the ends), there is a limiting stoichiometry of C_2F for which the fluorinated tube can still maintain its tube-like (albeit puckered) structure. This is supported by the product stoichiometries obtained via elemental analysis and the evidence of significant tube destruction at fluorination temperatures greater than 325° C. Further addition of fluorine would then lead to the breaking of carbon-carbon bonds and, hence, destruction of the tube. Accordingly, this invention provides a method of derivatizing SWNT with F_2 to add fluorine substituents to the exterior of the sidewalls in stoichiometries of up to C_2F, although lesser amounts of fluorine can also be attached by further diluting the fluorine or by lowering the reaction temperature.

Changing the Derivatization of SWNT by Fluorine Substitution

Because the inertness of the SWNT side wall approximates that of the basal plane of graphite, chemistry involving the SWNT side wall may be quite limited. However, the present invention provides methods for fluorination of single wall carbon nanotubes (SWNT) where fluorine is covalently bound to the side wall of the nanotube and thus provide sites for chemical reactions to occur. Functionalization via a fluorinated precursor may thus provide an attractive route to a wide range of side wall derivatizations.

In a particular embodiment, highly purified single wall carbon nanotubes (SWNTs) may be fluorinated to form "fluorotubes" which can then be solvated as individual tubes. For example, fluorotubes may be solvated in various alcohol solvents via ultrasonication. The solvation of individual fluorotubes has been verified by dispersing the solvated tubes on a mica substrate and examining them with

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atomic force microscopy (AFM). Elemental analysis of the tubes reveals that light sonication in alcohol solvents does not remove significant amounts of the fluorine. These solutions will persist long enough (over a week) to permit solution phase chemistry to be carried out on the fluorotubes. For example, the solvated fluorotubes can be treated with hydrazine to remove fluorine, leading to precipitation from solution of normal, unfluorinated SWNTs. Alternatively, fluorotubes can be reacted with sodium methoxide to yield methoxylated SWNTs. These reaction products have also been characterized by elemental analysis and a variety of spectroscopies and microscopies.

The present inventors have, for the first time, functionalized the sidewalls of SWNTs by reacting them with elemental fluorine. The inventors have discovered that fluorine could be added to the side wall of carbon nanotubes yielding stoichiometries up to approximately C_2F without destruction of the tube-like structure. The inventors have also discovered that a high degree of solvation can be achieved by sonicating fluorinated SWNTs in a variety of alcohol solvents such as methanol, ethanol, and isopropanol. As demonstrated herein, reactions can be carried out on these nanotubes while in solution by reacting them with hydrazine which serves as a defluorinating agent. It has also been demonstrated that these "fluorotubes" can be reacted with sodium methoxide (a strong nucleophile) while in solution to form methoxylated SWNTs.

The inventors have shown that single wall carbon nanotubes can be fluorinated and then sonicated in alcohols to form stable solutions of fluorotubes. This solvation allows one to manipulate the fluorotubes in ways that were previously unavailable and opens the door to a wide variety of possibilities with respect to exploring the physical and chemical properties of fluorotubes. "Tuning" the fluorine content of a fluorotube by first fluorinating it heterogeneously, solvating it in an alcohol, and then defluorinating it with substoichiometric quantities of hydrazine is consequently available as a way of making a wide variety of fluorotubes with differing fluorine contents and in some instances quite different properties.

The inventors have further demonstrated that once solvated, these fluorotubes can then be reacted with species while in solution to either defluorinate or further functionalize them. The chemistry possible with these solvated fluorotubes provides an important route to the synthesis of a wide variety of functionalized nanotubes having many different and useful properties.

An exemplary derivatization is the methylation of SWNT. Methylated SWNT are the product of the nucleophilic substitution of fluorine (attached to the SWNT side wall) by the methyl groups in methyl lithium. Nucleophilic substitution of this type has been previously reported for the reaction between fluorinated C_{60} and alkyl lithium species (Taylor, et al., 1992). The C—F bonds in fullerene cages and tubes are weakened relative to C—F bonds in alkyl fluorides by an eclipsing strain effect (Taylor, 1998 *Russian Chem. Bull.,* 47:823–832). This renders the bonds more susceptible to nucleophilic attack. A normal S_N2 process is geometrically impossible and a S_N1 process would be extremely unlikely, so either a novel front side displacement or possibly an addition-elimination process is responsible for the nucleophilic substitution (See Taylor, 1995, in "The Chemistry of Fullerenes," R. Taylor, ed., world Scientific Publishing, London, pp.208–209).

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correspond to sp^3 and sp^2 carbon stretching modes, respectively. At higher reaction temps, yielding high F to C ratios, these peaks disappear and the fluorescence is attenuated. As C—F bonds are not very polarizable, it is understandable that they are not seen in the Raman spectra presented here.

Raman spectra of the defluorinated products of the SWNT originally fluorinated at 250° C., 325° C. and 400° C. are shown in FIG. 4. Traces A, B and C correspond to the material originally fluorinated at 250° C., 325° C. and 400° C., respectively. As can be seen in traces A and B, the characteristic breathing mode at 186 cm^{-1} returns upon defluorination. This is not true in trace C, indicating that the tubes are largely destroyed at 400° C. Additionally, the peak at 1340 cm^{-1} grows relative to the characteristic SWNT peaks with increasing fluorination temperature. This can be attributed to one or both of the following factors: one, tubes are being "funzipped" much more readily at the higher temperatures and secondly, at higher reaction temperatures, a greater amount of decomposition of the type: CF_4, C_2F_4, C_2F_6, etc, is occurring SEM images and two-point resistivity measurements were obtained on a single piece of "bucky paper" after each of the following stages: purification, fluorination at 325° C. and defluorination in hydrazine at room temperature for one hour. FIG. 5-A shows the purified starting material. FIG. 5-B shows the same piece after having been fluorinated at 325° C. for 5 hours. The image shows excessive charging due to its insulating nature, but the "rope-like" structure of tubes is still evident. Finally, FIG. 5-C shows the same piece of "bucky paper" after having been defluorinated in hydrazine. The two-point resistance of the purified starting material is 15–16Ω measured 5 mm across the surface of the "bucky paper". Identical measurements on the fluorinated and defluorinated "bucky paper" yielded a resistance of >20 MΩ and 125–130Ω respectively. It is interesting to note that the defluorinated material recovers most, but not all of its original conductivity.

Example 2

2.1 Preparation of Fluorinated Single-wall Carbon Nanotubes

SWNT were produced by the dual pulsed laser vaporization of Co/Ni doped graphite rods and purified as discussed previously (Rinzler, et al., 1998). The highly purified product consists of colloidally suspended bundles or "ropes" of SWNT (Liu, et al., 1998). Filtering this over a 0.2 micron PTFE filter membrane and rinsing with methanol yields a black film that can be peeled off to give a freestanding "bucky paper." This paper was then oven baked for several hours at 150° C. to remove any residual solvent. The baked "bucky paper" was then loaded into a temperature controlled monel flow reactor where it was purged at 250° C. under a stream of He for ~1 hour. A 10% F_2 in He mixture was then passed over the sample after first being passed over NaF to remove any HF present. This yielded material with stoichiometrics ranging from C_3F to C_2F (as determined by electron microprobe analysis) depending on reaction time (between 8 and 12 hours) and on the quantity being fluorinated.

2.2 Methylated Single-wall Carbon Nanotubes

Once fluorinated, the nanotubes were then placed in a reaction flask under a N_2 purge. Methyl lithium (1.4 M in diethyl ether, Aldrich) was then added in significant molar excess via syringe through a rubber septum in the reaction flask. The reaction mixture was then refluxed for three hours and after which, the methyl lithium was neutralized with a water/ether mixture. The resulting material was then filtered, washed with 3M HCl (to remove LiF and LiOH) followed by methanol and then oven dried at 130° C. Electron

microprobe analysis revealed the fluorine content of this material to be 3.7 atomic percent (down from around 30%). SEM and TEM analysis confirmed that the rope and tube structures survived both the fluorination and methylation steps.

The Raman spectroscopy of SWNT is now well known (Rao, et al., 1998). Raman spectroscopy of the methylated nanotube product was obtained on a Spex Triplemate spectrometer equipped with a CCD detector and using a 514.5 nm Ar laser excitation source. The spectrum reveals that significant alteration has taken place (FIG. 6). Pyrolysis of this material in Ar at 700° C. regenerates the original SWNT as evidenced by its Raman spectrum. TGA of the pyrolysis process reveals a 25% mass loss upon heating to 700° C. EI mass spectroscopy of the pyrolysis products reveals CH_3 groups to be the major species being evolved during the pyrolysis (FIG. 7) with the rest of the mass peaks being consistent with methyl recombination pathways during pyrolysis.

The electrical properties of the SWNT change dramatically as they are functionalized. The untreated SWNT are essentially metallic and their two point resistance (essentially a contact resistance, Bozhko, et al., 1998, Appl. Phys. A, 67:75–77) measured across 5 mm of the "bucky paper" surface is 10–15Ω. When fluorinated, the tubes become insulating and the two point resistance exceeds 20 MΩ. After methylation the tubes possess a two point resistance of ~20 kΩ. Pyrolysis of the methylated product brings the resistance down to ~100 Ω. Incomplete return of the electrical conductivity upon pyrolysis may be due to an increased contact resistance that results from disorder induced into the rope lattice following the sequence of reaction steps.

The methylated SWNT could be suspended quite readily by sonication in chloroform. Dispersal of this suspension on a Si wafer followed by AFM analysis confirmed the nondestructive nature of the sonication process. Additionally, a large number of single tubes could be seen. This was not true of similarly exposed, untreated SWNT.

To get an infrared spectrum of the product, the dried methylated material was suspended in $CDCl_3$ and dispersed over KBr powder which was then dried and pressed into a pellet. By using deuterated chloroform we eliminated the possibility of seeing C—H stretching modes due to the presence of residual solvent. IR analysis of the pellet revealed a significant amount of C—H stretching in the ~2950 cm^{-1} region of the spectrum as shown in FIG. 8. Also present, however, is a significant C—F stretching band indicating that not all of the fluorine had been displaced. This might be because the bulky methyl lithium cannot penetrate the rope lattice to the extent that the fluorine could in the original fluorination. Alternatively, the cage is likely to become less electronegative and, therefore, less susceptible to nucleophilic attack as successive fluorines are displaced (see Boltalina, et al., 1996, J. Chem. Soc., Perkin Trans., 2:2275–2278).

The methylated tubes were not suspendable in any of the nonpolar hydrocarbon solvents tried, although not all possibilities were investigated. The fact that the suspendability of the methylated tubes in $CHCl_3$ is superior to that of the untreated tubes is interesting, however. Using a suitable solvent to suspend the methylated SWNT as individual tubes capable of being manipulated individually, will have significant benefits. Alternatively, other nucleophiles, e.g. butyl, can be substituted for the fluorine to render the SWNT more suspendable in a suitable solvent, which is equally significant.

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In summary, SWNT were methylated by first fluorinating them and then reacting the fluorinated product with methyl lithium. This methylation of fluorinated SWNT precursors proceeds through a novel nucleophilic substitution pathway that is capable of generating a wide range of substituted SWNT products.

Example 3

3.1 Preparation of Highly Purified SWNTs

Single wall carbon nanotubes were produced by the dual pulsed laser vaporization of Co/Ni doped graphite rods and purified by methods discussed previously (Rinzler, et al., Appl. Phys.A, 1998, 67:9–37.). The SWNTs produced in this way are primarily (10,10) nanotubes. The purified product is a metastable colloidal suspension of SWNT "ropes" (bundles of tubes ranging from a few to 200 SWNTs, see Thess, et al., Science 1996, 273, 483–487) in a 0.2% aqueous solution of Triton™ X-100 surfactant. This was then filtered over a PTFE filter membrane (Sartorius, with 0.2 μm pore dimensions) and rinsed with methanol. Filtering this and rinsing with methanol leads to a final product which is a freestanding "mat" or "bucky paper" of SWNTs that is approximately 10 μm thick. Purity of the SWNTs was monitored via scanning electron microscopy (JEOL 6320F SEM). FIG. 9 shows a sample of typical purity. This product was then resuspended by sonication in dimethyl formamide (DMF; Fisher, HPLC grade). Such treatment is believed to "cut" the tubes at their defect sites and also seems to unravel the ropes somewhat, leading to bundles containing fewer SWNTs. This product was then filtered, rinsed and heated in an oven at 150° C. for 2 hours prior to fluorination. Sonication in DMF may result in smaller SWNT ropes and ultimately lead to a more efficient fluorination.

3.2 Preparation of Fluorinated SWNTs

The purified nanotubes (5–10 mg in the form of bucky paper) were placed in a temperature controlled fluorination reactor constructed of Monel™ and nickel. After sufficient purging in He (Trigas 99.995%) at 250° C., fluorine (Air Products 98%, purified of HF by passing it over NaF pellets) was introduced. The fluorine flow was gradually increased to a flow rate of 2 sccm diluted in a He flow of 20 sccm. The fluorination was allowed to proceed for approximately 10 hours, at which point the reactor was brought to room temperature, and the fluorine flow was gradually lowered. After the fluorine flow was completely halted, the reactor was purged at room temperature for approximately 30 minutes before removing the fluorinated product. The fluorinated SWNTs consisted of approximately 70 atomic percent carbon and 30 atomic percent fluorine as determined by electron microprobe analysis (EMPA, Cameca SX-50). This fluorinated product was well characterized with Raman, IR, SEM, TEM, resistance measurements and x-ray photoelectron spectroscopy (Physical Electronics PHI 5700 XPS using soft monochromatic Al Ka (1486.7 eV) x-rays).

3.3 Solvation in Alcohols

Attempts to solubilize fluorotubes with the "like dissolves like" approach of sonicating and heating them in perfluorinated solvents met with little success. Attempts were also made to solvate them in hydrogen bonding solvents. Recent studies on the hydrogen bonding capabilities of alkyl fluorides suggest that the fluorine in such species are poor hydrogen bond acceptors (Dunitz, et al., R, Eur. J. Chem., 1997, 3(1):89–98; Howard, et al., Tetrahedron, 1996, 52(38): 12613–12622). The F ion, however, is one of the best hydrogen bond acceptors available. The strength of the hydrogen bond formed between HF and F approximates that of a covalent bond (Harrell, et al., JACS 1964, 86:4497). An

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XPS analysis of our fluorinated SWNT product reveals an F Is peak at a binding energy of 687 eV. Polytetrafluoroethylene has an F is binding energy of 691.5 eV. This suggests that the fluorine bonded to the fluorotubes is considerably more ionic than the fluorine present in alkyl fluorides (see Watanabe, et al., Graphite Fluorides, Elsevier: Amsterdam, 1988; p.246). Thus, the increased ionic nature of the C—F bond in the fluorotubes may make the fluorine on it better hydrogen bond acceptors.

Sonication of the fluorinated SWNT material in alcohols was carried out by placing approximately 1 milligram of material into a vial containing approximately 10 mL of alcohol solvent and sonicating for approximately 10 minutes. Sonication was performed by partially immersing the capped vial in a Cole-Parmer ultrasonic cleaner (containing water) operating at 55 kHz. The solvated fluorotubes were then dispersed on a clean mica surface by means of a 3000 rpm rotary spinner (Headway Research, Inc.) and examined with atomic force microscopy (Digital Instruments Multimode SPM). The solvated fluorotubes were also analyzed with a Shimadzu model 1601PC UV-vis spectrometer using quartz cuvetts.

Fluorotubes were solvated by sonicating in alcohol solvents including: methanol, ethanol, 2,2,2-trifluoroethanol, 2-propanol, 2-butanol, n-pentanol, n-hexanol, cyclohexanol and n-heptanol. Sonicating the fluorotubes in alcohol solvents produced metastable solutions. These solutions were stable for a couple of days to over one week, depending on the concentration and solvent used. While typical sonication times were around 10 minutes, the heavier solvents (pentanol and up) required slightly longer sonication times in order to fully suspend the tubes. Of the solvents used, 2-propanol and 2-butanol seemed to solvate the fluorotubes the best with the solutions being stable for more than a week. The solubility limit of the solvated "fluorotubes" in 2-propanol is at least 0.1 mg/mL. This solution was stable for slightly less than a week with some particulate matter precipitating out after a few days. This suggests that pushing the solubility limit somewhat decreases the solution's stability or that a super saturated solution can exist for a shorter period of time. All of the other solutions were stable for at least a couple of days before the onset of precipitation. A likely scenario for such solvation would be hydrogen bonding between the alcohol's hydroxyl hydrogen and the nanotubebound fluorine (scheme 1). No evidence of alkoxy substitution (or evolution of HF) was observed.

Scheme 1
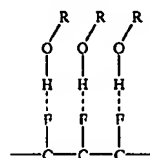
Efforts were also made to solvate the fluorotubes in other strong hydrogen bonding solvents like water, diethyl amine, acetic acid and chloroform. While water will not "wet" the fluorotube by itself, it will with the addition of a small amount of acetone. Still, even long sonication times in this water/acetone mixture failed to solvate the fluorotubes. Likewise, neither diethylamine nor acetic acid would solvate the fluorotubes. Chloroform solvated the tubes, but the solution was far less stable than those in alcohol solvents, with the fluorotubes falling out of solution in less than an hour.

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The Grignard reaction is thus an example of the typical reaction of aldehydes and ketones: nucleophilic addition.

But this is only half the story. Not only does the Grignard synthesis involve formation of a carbon–carbon bond, but the product contains the highly versatile group —OH. And now, as we shall soon see, the way is open to further synthesis, and the building of still bigger and more complicated structures.

Products of the Grignard synthesis

The class of alcohol that is obtained from a Grignard synthesis depends upon the type of carbonyl compound used: *formaldehyde*, HCHO, *yields primary alcohols*; *other aldehydes*, RCHO, *yield secondary alcohols*; and *ketones*, R_2CO, *yield tertiary alcohols*:
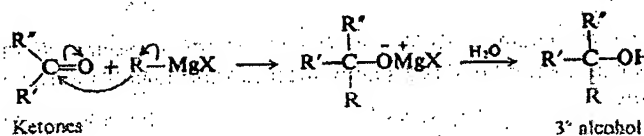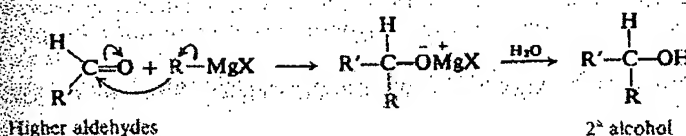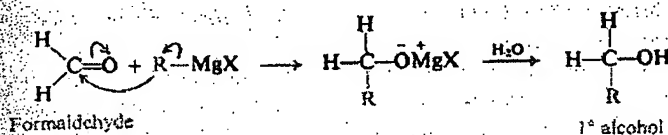
This relationship arises directly from our definitions of aldehydes and ketones, and our definitions of primary, secondary, and tertiary alcohols. The number of hydrogens attached to the carbonyl carbon defines the carbonyl compound as formaldehyde, higher aldehyde, or ketone. The carbonyl carbon is the one that finally bears the —OH group in the product; here the number of hydrogens defines the alcohol as primary, secondary, or tertiary. For example: